

X-RAY AND ELECTRON DAMAGE, AND PHOTOCHEMICAL REACTIONS
IN CdS SINGLE CRYSTALS AND LAYERS, AND
ANNEALING OF THESE DEFECTS

SEMI-ANNUAL PROGRESS REPORT
July 1, 1964 - December 31, 1964

Grant
~~Contract~~ No. NsG-573
National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

UNPUBLISHED PRELIMINARY DATA

GPO PRICE \$ _____

OTS PRICE(S) \$ _____

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Hard copy (HC) 3.00

Microfiche (MF) 50

FACILITY FORM 802	N65 17505	
	(ACCESSION NUMBER)	(THRU)
	<u>56</u>	<u>1</u>
	(PAGES)	(CODE)
	<u>CL 60866</u>	<u>26</u>
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

17505

The work done in connection with this contract in the second half year was as follows:

1. Growing of CdS single crystals by sublimation technique (for further details see first progress report.)
2. Evaporation of metal contact layers onto CdS in very high vacuum.
3. Further investigations of the level distribution in the band gap of the CdS single crystals using glow curves and spectral distribution of photoconductivity after heat treatment of CdS crystals in ultra-high vacuum.
4. Further investigations of the change in level distribution of CdS after irradiation with x-rays between 100 and 300 keV in ultra-high vacuum.
5. Further investigations of electrical properties of CdS crystals during heat treatment in sulfur vapor at temperatures between 300° and 750°C.
6. Further investigations of the change of optical absorption spectrum of large CdS crystals after irradiation with electrons in the 2 to 8 MeV range were suspended since the student who was assigned to that program was not available during the first semester of the academic year 1964 to 1965.

author

Ad 2:

Work is being conducted in an attempt to produce ohmic contacts on CdS single crystals. The particular method that is being investigated is the double layer electrode. A double layer electrode is produced by evaporating under ultra-high vacuum conditions successive layers of first, aluminum or indium - then gold.

Three to five crystals at a time are prepared for a double layer evaporation. Two electrode areas ($\sim 10\text{mm}^2$) spaced .7mm apart are left bare - the rest of the crystal being masked. Measured amounts of the two metals to be used are placed in tungsten evaporation baskets and the CdS substrate holder is mounted in the vacuum system a given distance from the evaporation source. The vacuum system is taken down to 10^{-7} torr, at which time the electrode metals are successively deposited on the CdS crystals.

The "ohmicness" of the electrode contact is tested by running current vs. voltage curves on each of the crystals; green light of fixed intensity is used to illuminate the crystal. Also, contact noise measurements are made - the less the contact noise measured, the better the electrical contact. Other measurements made on the crystals include relative photosensitivity and dark current.

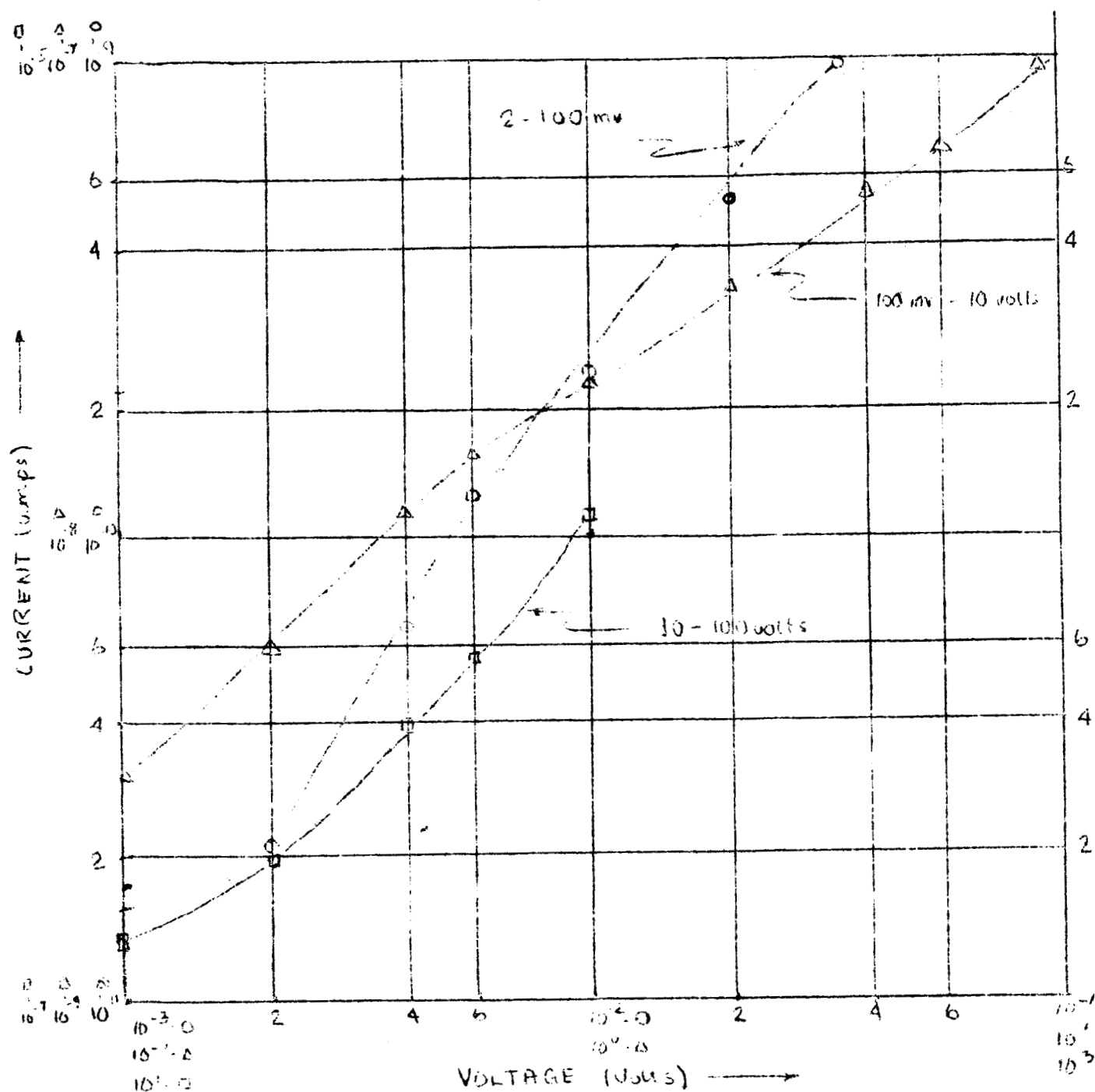
In an attempt to determine the relative quality of the aluminum and indium as ohmic contact metals, a crystal will be split in half. On one half of the

original crystal In-Au electrodes are deposited, on the other half of the original, Al-Au electrodes. So far, the results have proved successful, a good percentage of both types of crystal contacts being prepared by this method testing out as ohmic. Interesting questions still to be resolved are:

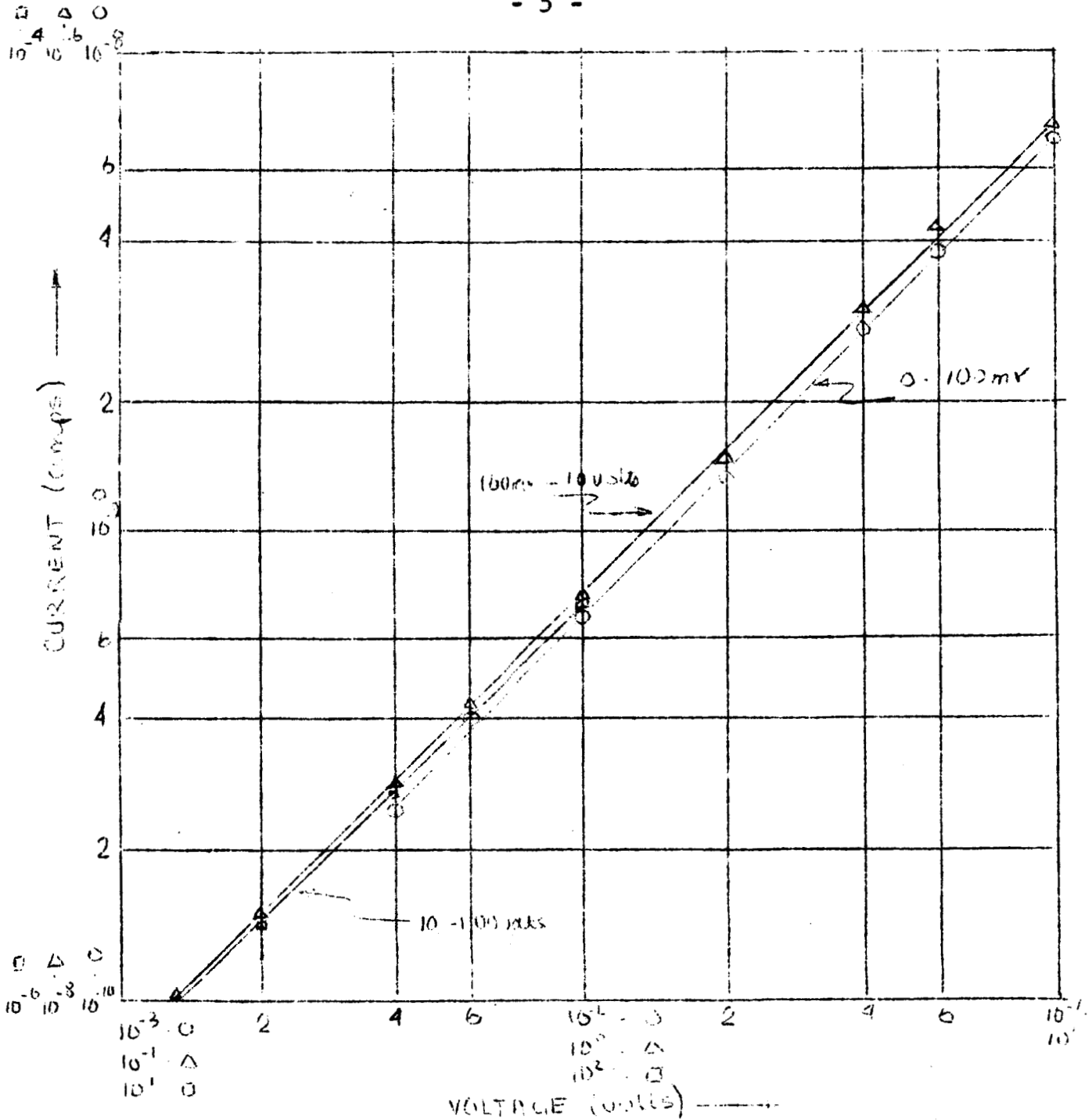
(1) the optimum amounts of the two electrode metals to be used to produce ohmic contacts,

(2) the dependence of the "ohmicness" of the contact as functions of time and temperature, and

(3) some interesting effects observed when measuring either photocurrent or photovoltage as a function of intensity with no applied voltage. One such anomalous effect is the reversal of photocurrent direction with an increase of intensity - but only for green light.



Current vs. voltage curve for a Al-Au double layer electrode; green light of constant intensity illuminating the crystal. The irregularity of this curve plus very detectable contact noise indicate the contact was non-ohmic. The contact (2:1 ratio by volume of Au to Al) was about 50% transparent.



Current vs. voltage curve for Al - Au double layer electrode; green light of constant intensity illuminating the crystal. The linearity of this curve plus no detectable contact noise demonstrate characteristics of an ohmic contact. The contact 8:1 ratio by volume of Au to Al was not transparent.

EFFECTS OF THERMAL DISORDERS IN CdS CRYSTALS ON SPECTRAL RESPONSE AND GLOW CURVE MEASUREMENTS

Ad 3:

Investigations have been made of two CdS crystals, which were not exposed to x-rays, for the effects of thermally induced disorders.

A general rise of the spectral response curve with increased heat treatment temperature was observed. Such a rise when combined with the fact that the spectral response curves do not change shape can be explained in terms of a decrease in the density of recombination centers and/or an increase in hole traps. In addition some changes in relative heights of the glow peaks indicate the formation of electron traps. One crystal was subjected to a long-time heat treatment in high vacuum and long-time changes in photo-response and glow curves are discussed in terms of surface desorption.

Experimental Procedure

The crystal is mounted in ultra-high vacuum ($\sim 10^{-10}$ to 10^{-11} Torr). The current through the crystal and the voltage across it are measured via the four electrode method.

The crystal is then heat treated in the dark at 100°C for one hour, during which time a certain degree of thermal disorder will occur, and then rapidly cooled to room temperature. The rapid cooling has the effect of freezing-in the disorder. A

spectral response curve is then run at room temperature followed by a glow curve. The crystal is then subjected to a 150°C heat treatment followed by the aforementioned measurements. This procedure is repeated for the heat treatments in 50°C steps up to 350°C.

After the 350°C measurements have been taken the crystal is annealed from 350°C to 25°C over a 10 hour period according to a prescribed schedule which was the same for both crystals.

The entire aforementioned program is then repeated several times in order to verify reproducibility and observe changes which might occur due to the long-time heat treatment of the crystal by several such programs.

Results

A. A Typical Program:

I.) Spectral Response Curves

A typical set of spectral response curves is shown in Figure 3-1. These exhibit a general rise in photo-current with increasing heat treatment temperature. There is a more pronounced increase in the extrinsic ($\lambda > 520\text{m}\mu$) side. There is no apparent change in shape of the curves (i.e. no new peaks appear.)

II.) Glow Curves

Figures 3-2 and 3-3 show typical glow curves (510m μ irradiation) for two different crystals. Both exhibit a general increase in current with increasing heat treatment temperature. Crystal #1 (Figure 3-2) shows almost no change in relative densities of

trapping levels. Crystal #2 (Figure 3-3) exhibits some growth of peaks at 0.35ev. and 0.67ev. and 0.78ev.

Considering both crystals; peaks are seen at 180°K (0.35ev.), 350°K(0.67ev.), 390°K(0.78ev.), and 440°C(0.85ev.).

Some investigations were made of the effects of 650m μ irradiation on the glow curves. The results were that there was no noticeable effect with crystal #1 and a considerable effect with crystal #2. Figure 3-4 shows a comparison of the 300°C glow curve for 510m μ and 650m μ irradiation of crystal #2.

B Changes over Several Programs

I.) Spectral Response Curves

Figure 3-5 shows the changes occurring over a period of nine months during which were performed eight programs. The change is characterized by a significant rise in photocurrent on the intrinsic ($\lambda < 520m\mu$) side.

Another trend which has appeared in the two crystals involves the appearance (after approximately two programs) of a pronounced jump in the extrinsic range between the 200°C and the 250°C curves as shown in Figure 3-6. This jump tended to vanish after still more programs were run.

II.) Glow Curves

Figure 3-7 shows the 300°C glow curve for crystal #1 over a nine month period. This shows a general loss of pronounced maxima in the glow curves. The 0.35ev. glow peak is greatly reduced while the 0.85ev. peak is increased.

Discussion of Results

A. A Typical Program

I.) Spectral Response Curves

A typical set of spectral response curves is shown in Figure 3-1. The fact that there is no apparent change in the

shape of the curves in the extrinsic ($\lambda > 520\text{m}\mu$) range indicates either that there is a uniform increase in the density of levels in the forbidden gap from which electrons can be excited or that the actual densities of these levels are relatively unchanged - the rise being attributed to increase of deep hole traps and/or decrease of recombination centers. The uniform increase, it is felt, is not very probable since there are probably certain preferred disorders which would be more readily formed contributing more levels of one energy than another. The existence of the parallel shift can then be attributed to an increase in the density of deep hole traps and/or a decrease in the density of recombination centers.

An argument can be given which could explain with some simplicity the higher extrinsic rise if one assumes that the effect of heat treatment is to destroy, by dissociation, a certain number of recombination centers per unit volume uniformly throughout the crystal. Let us then consider diagram #1. Assume for simplicity that there is a uniform distribution of levels throughout the crystal. There will then, in general, be a larger density of recombination centers in the near surface region (say 10^{17}cm^{-3}), due to the greater separation of the quasi-fermi levels E_{fn} and E_{fp} , than in the volume where we assume 10^{16}cm^{-3} . Removal of 5×10^{15} levels cm^{-3} (as shown) would result in a small change of the near surface recombination rate while the bulk recombination rate would be greatly (~50%) reduced. This would cause a higher extrinsic rise. This

behavior is not easily explainable with the other proposal of increased density of deep hole traps. Thus the proposed mechanisms of decrease of recombination centers deeply seems to be the most plausible explanation.

NEAR SURFACE		BULK	
Before Heat	After heat	Before heat	After heat
E_{fn}			E_{fn}
$10^{-17}/cm^3$	$9.5 \times 10^{16}/cm^3$	$10^{16}/cm^3$	$5 \times 10^{15}/cm^3$
E_{fp}			E_{fp}

Diagram 3-1

To a first approximation, recombination centers lie between E_{fn} and E_{fp}

II Glow Curves

The general rise of the glow curves once again indicates the possibility of breaking up recombination centers. The fact that crystal #1 (figure 3-2) exhibits no significant peak growth over a single program suggests that the formation of electron traps is not responsible for this rise.

To a first approximation, the same is true for crystal #2 (Figure 3-3). There does appear, however, to be superimposed on the general rise, a change in peak structure indicating some increase in electron

traps at (0.35ev.), (0.67ev.) and (0.78ev.) some of which may indicate the energies of dissociated recombination centers.

The fact that Figure 3-4 shows a marked difference in the glow spectrum for 510m μ and 650m μ irradiation can possibly be explained in terms of the difference between trap distributions in the near surface (510m μ illumination) and bulk (650m μ illumination) regions.

The fact that no such effect was observed in crystal #1 may be an indication that the glow curves (both 510m μ and 650m μ) observed in that crystal were due to levels occurring predominantly in the near surface region.

B. Changes over Several Programs

I.) Spectral Response Curves

Over a nine month period during which crystal #1 was kept in a vacuum of 10^{-10} to 10^{-11} Torr during which it was subjected to eight programs, the general shape of the spectral response curves changed as shown in Figure 3-5. It is suspected that this change in the intrinsic ($\lambda < 510\text{m}\mu$) region is due to a decreased density of surface recombination centers. The fact that the photocurrent falls off in the intrinsic region has been attributed in part to the presence of surface recombination centers, which among other things are abundant because of impurities and the larger separation of the quasi-fermi levels there. After many high temperature ($\sim 350^\circ\text{C}$) treatments many of the surface impurities probably have been desorbed resulting in a decrease of surface recombination centers.

II. Glow Curves

The reduction of the 0.35ev. glow peak and the increase of the 0.85ev. peak over the nine month period is probably due to the passage of some type of imperfections or impurity out of the crystal. This trend was not dependent upon the irradiation wavelength and hence is possibly governed entirely by traps in the near surface region.

Figure 3-1

TYPICAL SPECTRAL
CRYSTAL #2

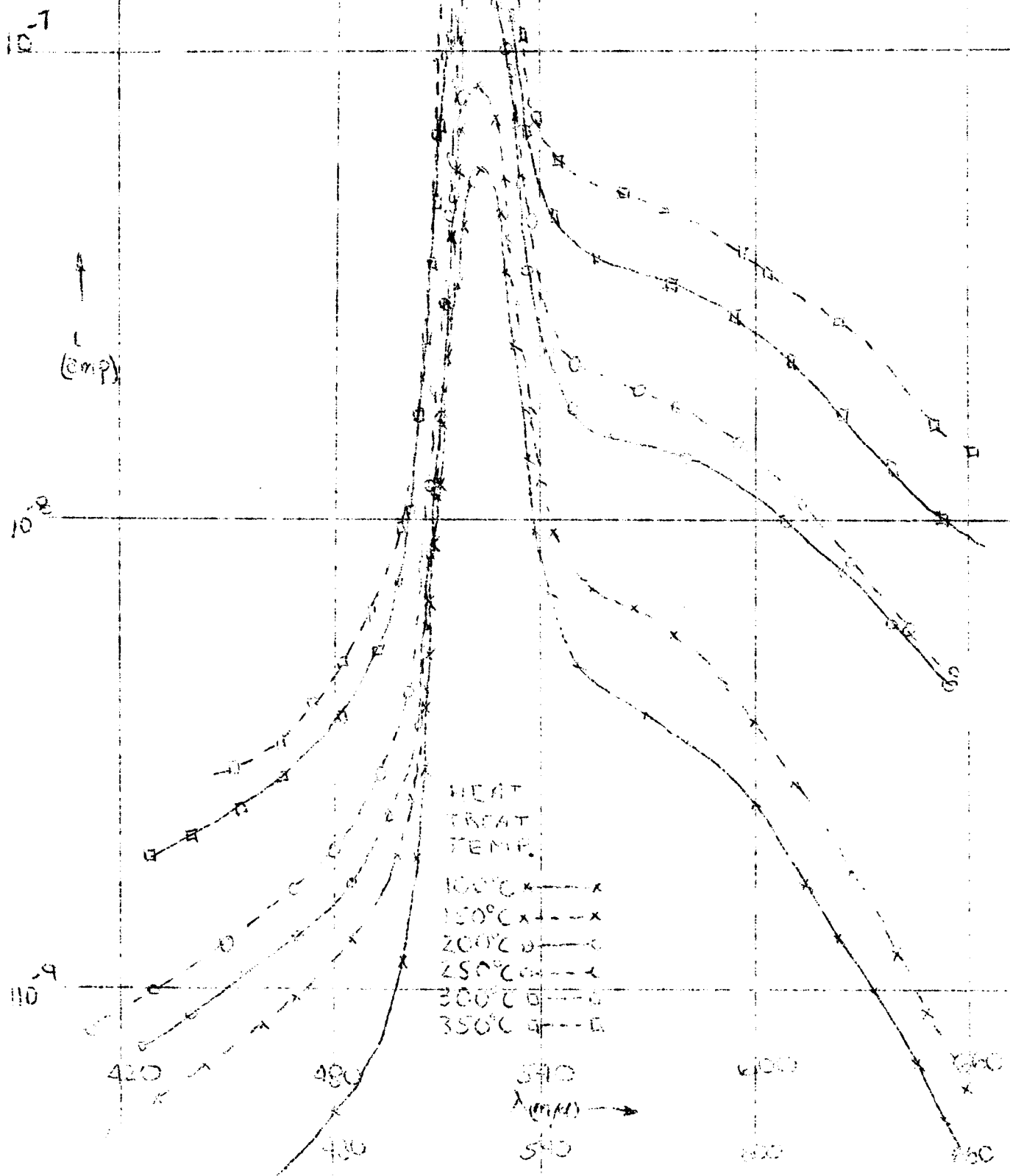


Figure 3-2

TYPICAL GLOW CURVE
CRYSTAL #1

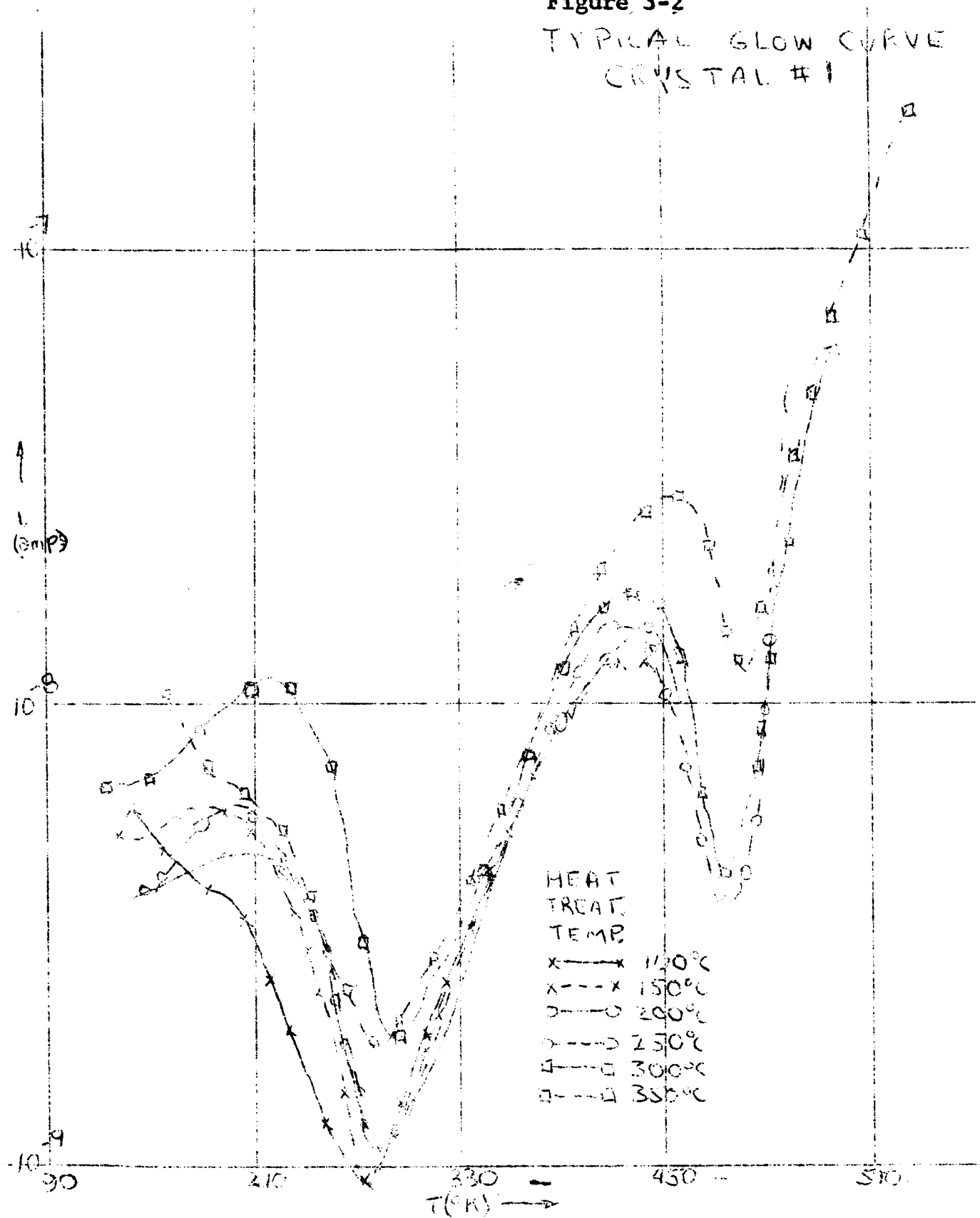


Figure 3-3

TYPICAL GLOW CURVE
CRYSTAL #2.

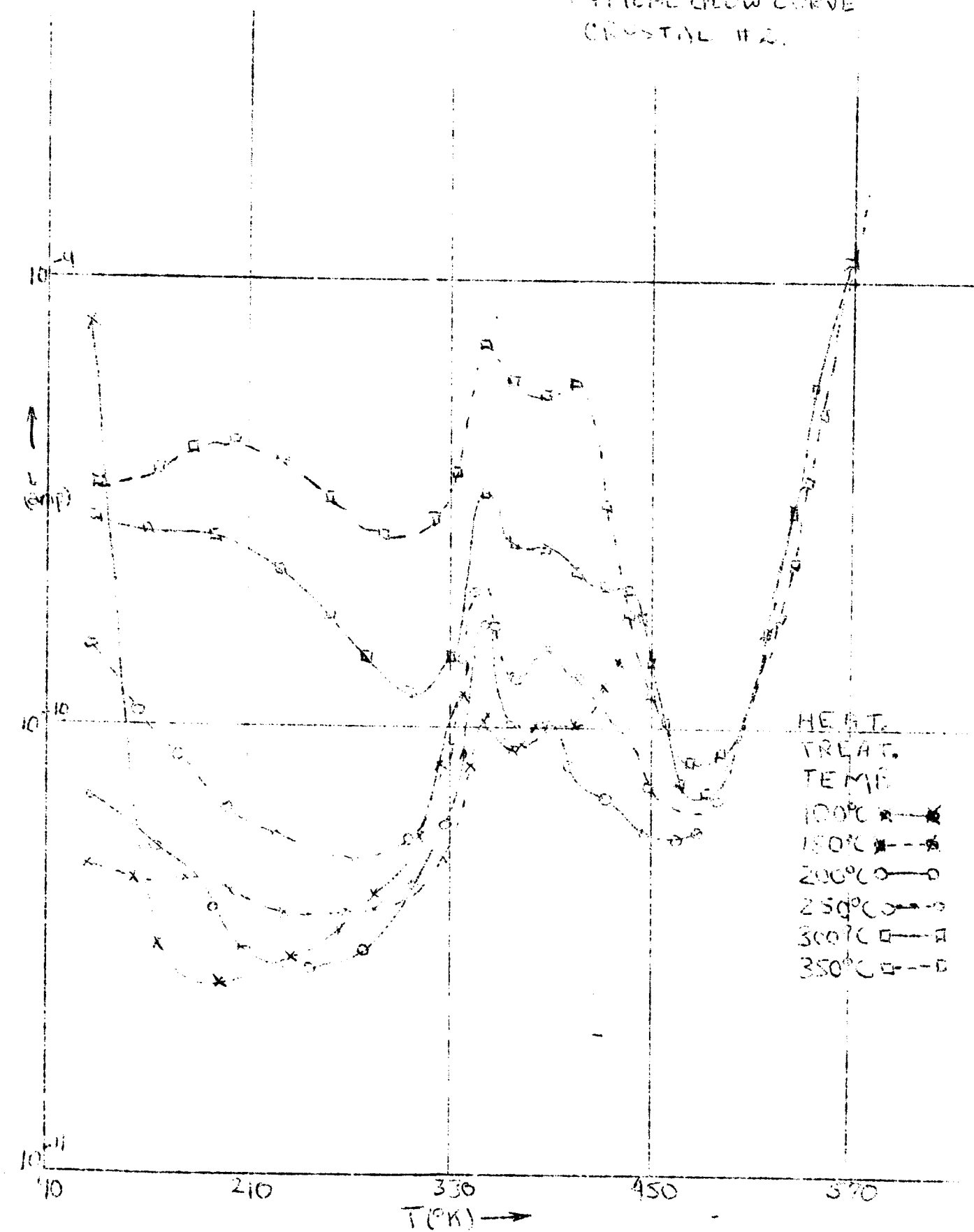


Figure 3-4

Comparison of 300°C Glow curves
with 510 mμ and 650 mμ irradiation
Crystal #2.

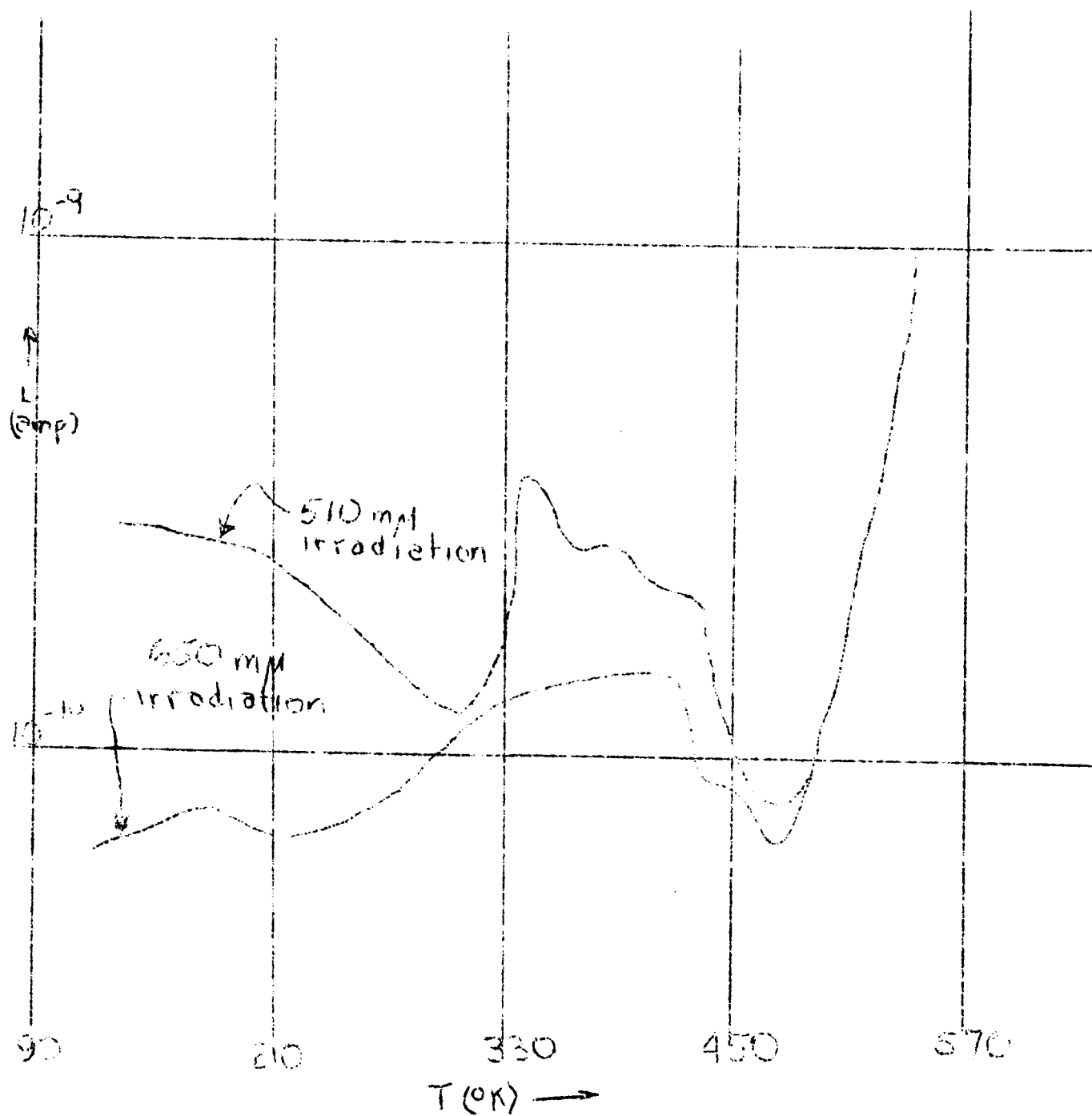


Figure 3-5

CHANGE IN
300°C Spectral
OVER 4 months
CRYSTAL #1

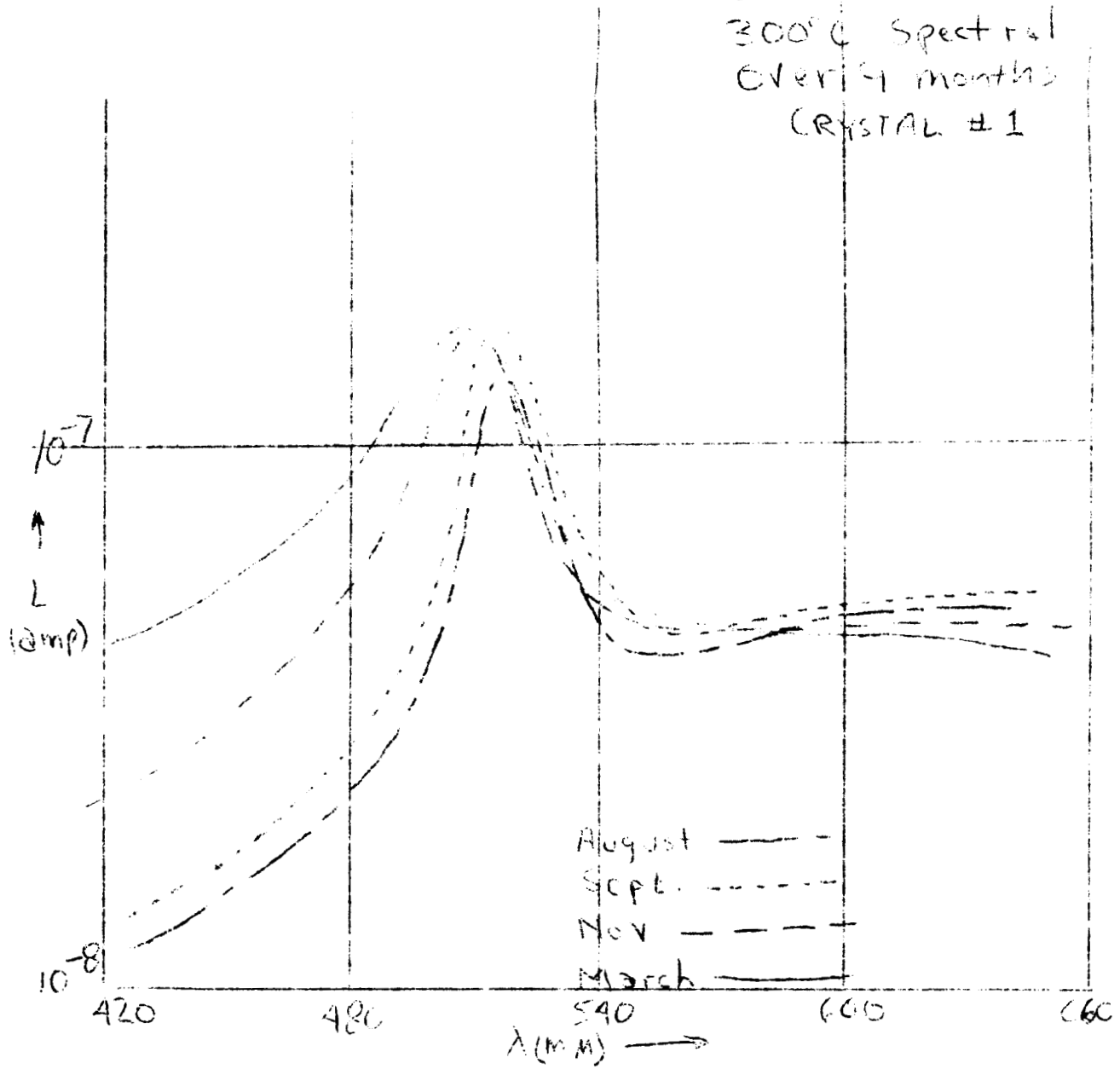


Figure 3-6
SHOWING
Extrinsic Jump
between 200°C
and 250°C curves

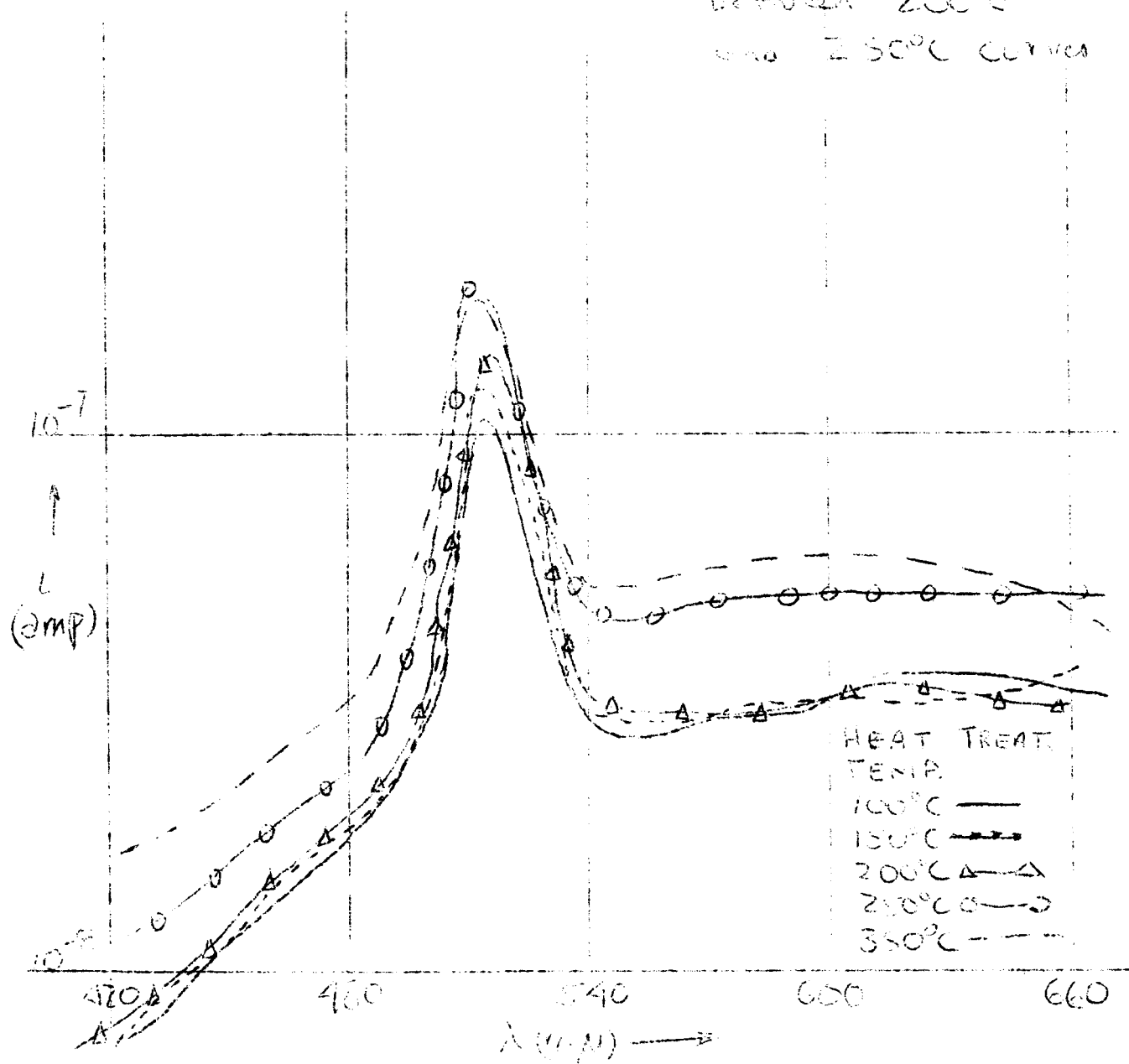
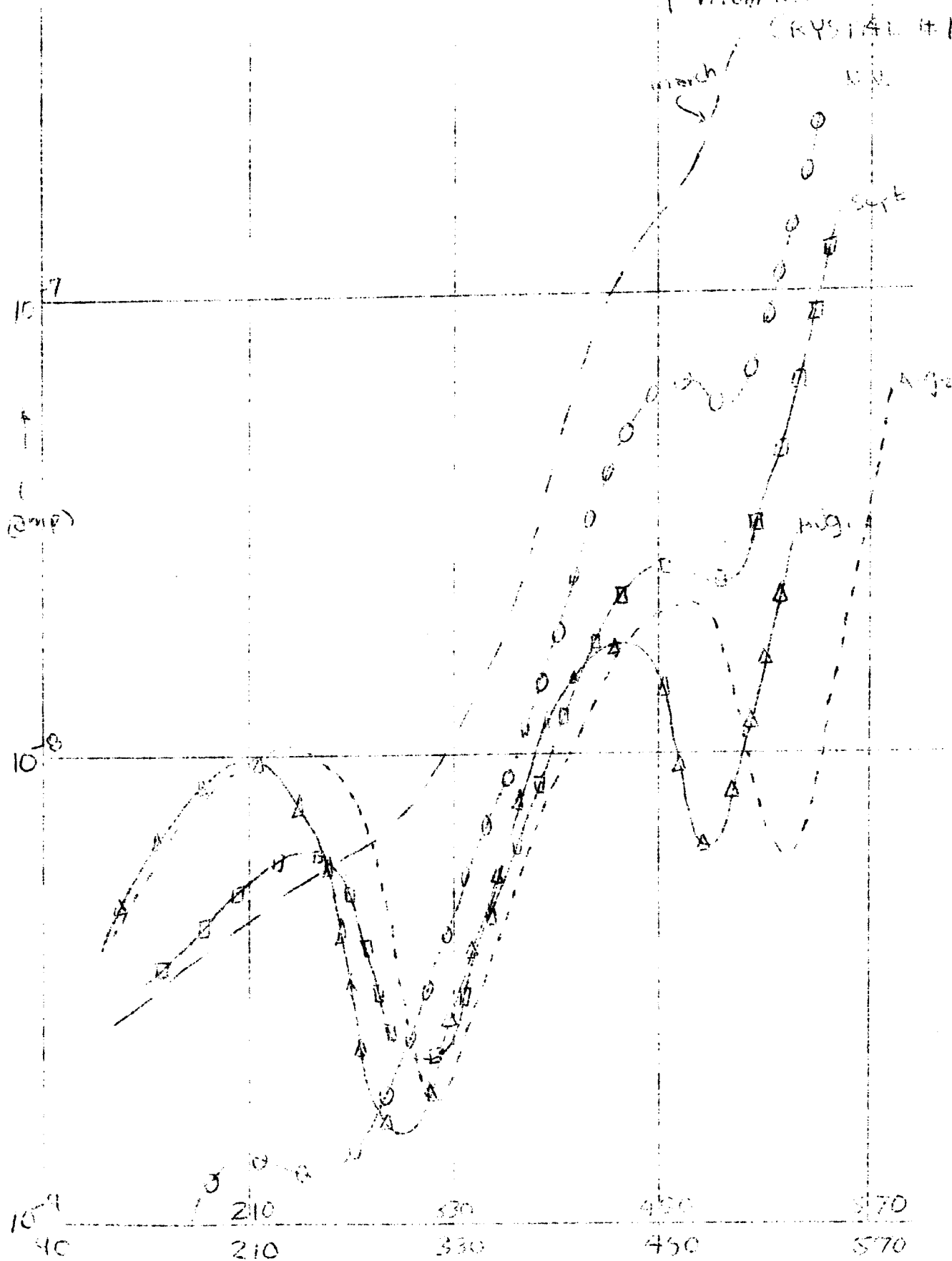


Figure 3-7
CHANGE IN 300°C
GLOW CURVE OVER
7 MONTHS
CRYSTAL #1



Ad:4

1. INTRODUCTION

It is well known that CdS monocrystals are sensitive to x-ray irradiation,^{1,2,3} although the complete processes which cause the increases and decreases in conductivity are not known. Since glow curves and the spectral response of photocurrents depend on the structure of the crystal, one obtains further information on the changes of the defect structure due to x-rays. Therefore an appropriate experimental arrangement has been assembled, initial data have been taken for the virgin crystal, x-ray irradiations at room temperature have been carried out, and annealing (to a certain extent) of the produced defects has been carried out.

2. Experimental Arrangement

The undoped CdS crystal (approximately 17 x 4 x 0.05mm) was provided with four evaporated electrodes of gold-chromium mixture. Two electrodes are used to pass a current through the entire crystal and the other two to measure the voltage at known points without drawing sufficient current to disturb the field. The crystal is held to a copper block by the pressure of the gold wires making contact with the electrodes, and insulated from the copper by a thin mica sheet. The temperature of the entire assembly can be varied by contact with liquid nitrogen or a heater and is measured by copper-constantan thermocouples. The crystal and holder are in a custom-made stainless-steel, ultra-high vacuum system with the necessary

connections to achieve and measure the pressure, regulate the temperature, make electrical connections, and shine visible light on the crystal. Ultra-high vacuum is deemed necessary to reduce the effects of gases ionized during x-ray irradiation.⁴

A Bausch and Lomb tungsten lamp monochromator supplies visible light to the crystal and is driven slowly enough (20mμ/hr), to achieve steady state values for spectral response measurements. Constant light intensity is assumed by rigid mounting of the monochromator, lens system, and crystal. A Keithley Model 413A micro-microammeter is in series with the crystal and a constant DC voltage supply to measure the current. Two Keithley Model 600A electrometers measure the voltage at the second two electrodes mentioned above. Current and voltage are recorded on Leeds & Northrup Speedomax recorders. A Minneapolis-Honeywell Rubicon Potentiometer measures thermocouple voltages.

3. Eperimental Results Initial Measurements

The crystal contacts were checked for rectification by measuring the current and reversing the electric field with light shining on it. Only a negligible amount was found. The vacuum system was now baked out and pumped down to the 10^{-11} torr range and has been kept below 10^{-10} torr continuously. During bakeout of the vacuum system at approximately 300° C the temperature of the

crystal was not allowed to exceed 190°C to prevent changes in defect structure from occurring.

Spectral response has been studied in the wavelength range of $440\text{m}\mu$ to $640\text{m}\mu$. Glow curve studies have been carried out for three different initial conditions:

1) Illumination at $510\text{m}\mu$ for 20 minutes after cooling the crystal to approximately -190°C .

2) Illumination at $650\text{m}\mu$ for 20 minutes and then cooling the crystal to approximately -190°C before running the glow curve.

3) The same as (1) except using $650\text{m}\mu$ for illumination.

4) The same as (2) except using $650\text{m}\mu$ for illumination.

The four different measurements were taken in various sequences to suit the experimental conditions.

Initial measurements were carried out twice in order to verify reproducibility: typical curves are shown in Figs 4-1 through 4-4. The spectral response shows itself to be typical of CdS with the peak being located at $520\text{m}\mu$.

The initial glow curves are seen to have a broad flat peak. This can be interpreted as the crystals having no dominant trap energy but rather a group or band of traps with an equivalent "thermal energy" range*

* $E \approx 25kT$

of 150°K to 270°K. A definite difference is seen between the curves of 510m_i irradiation and 650m_i irradiation; namely that the high energy end of the traps do not readily fill up at 510m_i irradiation. Traps that fill at room temperature but not at liquid nitrogen temperature and vice-versa do not appear to be present, since no noticable difference is seen between the glow curves at two irradiation temperatures; see figures 4-2 and 4-4

4. X-ray Irradiations

All x-ray irradiations were done at Frankford Arsenal in Philadelphia. Vacuum pressure was maintained during irradiation by the use of a titanium sublimation pump which was fired previous to transporting the vacuum chamber. Upon return the pressure was measured and found to be in the 10⁻¹⁰ torr range.

Constant x-ray dosage was achieved by holding the quantity $\frac{it}{r^2}$ constant at a value of $4 \frac{\text{ma-mm}}{\text{m}^2}$, where

i in ma is the x-ray current, t in min is the total time and r in inches is the distance from the cone tip of the x-ray machine to the crystal.

Immediately after x-ray irradiation the crystal temperature was reduced to approximately -190°C and held there until the first glow curve was run.

The changes in spectral response induced by x-rays are shown in Figure 1. A decrease in the conductance

at wavelengths longer than 525m μ and an increase for wavelengths shorter than 525m μ is seen for irradiation with x-rays of 150keV energy. As the x-ray energy is increased to 250keV the spectral response decreases and in the intrinsic range lies between the initial and 150keV value. The largest decreases occur over the entire spectral response after 300keV x-ray irradiation.

For 150keV and 250keV x-ray irradiation the glow curves changed less than 0.1 order of magnitude, as seen in Figs. 4-2, 4-3 and 4-4. However, for illumination at 510m μ the glow curves went up whereas for 650m μ illumination the glow curve decreases. For 300keV x-rays the largest changes were encountered, approximately one-half an order of magnitude. The conductance for 510m μ illuminated glow curve increased while the 650m μ glow curve decreased. The glow curves still have broad flat maximums.

4.1 Discussion of X-ray Effects

For simplicity all x-ray and temperature induced changes in the crystal will be assumed to arise from Cd and S only, and in the simplest possible way, i.e. intrinsic defects. We realize that in actual practice many more elements may be present in varying amounts but to determine which ones act as what type of center, their associated energy, and the probability of x-rays hitting the impurity is almost impossible at the present time.

4.2 Phenomenological Model

The postulation of three types of x-ray induced centers would account for the above mentioned changes.

a) Recombination centers whose probability of formation increases with increasing x-ray energy up to at least 300keV, and with a spatially inhomogeneous distribution with the highest density located in the bulk.

b) Hole traps which are produced already at x-ray energies below 150keV and whose probability of formulation increases less than the probability of forming recombination centers with increasing energy. These defects are predominantly produced near the surface, resulting in a spatially inhomogeneous distribution.

c) Electron traps which have an energy continuum but decrease in number as the trap energy increases and whose formation becomes more probable with increasing x-ray energy up to at least 300keV. These defects are also produced predominately near the surface.

The decrease in conductivity in the long wavelength side of the spectral response can be explained by an increased number of recombination centers.

a) At long wavelengths the absorption of light is quite uniform throughout the crystal, in turn the free electrons and non-conduction holes (n-type material assumed) caused by photons can recombine at the newly formed centers and reduce the photoconductivity. Superimposed in this process is the trapping of holes

which increases the electron conductivity. However, with a sufficient number of recombination centers present this is unseen. Then at shorter wavelengths more and more of the absorption takes place in the surface layer away from the higher density of recombination centers and even though we have more recombination centers due to a spread in the quasi-Fermi levels near the surface, the domination of the effect of trapped holes leads to the rise in photo-response as is seen in Figure 4-2. As the x-ray energy is increased the density of recombination centers increases faster than the hole trap density until the recombination centers control the entire range of the spectral response as is the case for all the 300keV x-ray irradiation.

The glow curves are completely explainable using postulates a, b, and c. As the density of recombination centers increases throughout the crystal with increasing x-ray energy one expects a decrease in the conductance as is true for 650m μ illumination glow curves (postulate a). However, near the surface an increase in the number of electron and hole traps with increasing x-ray energy will increase the conductance as is true for 510m μ illumination. The above statements do not contradict each other since in one case recombination centers and 650m μ light are used to explain bulk

properties whereas in the other case electron and hole traps and 510m μ light are used to explain a near surface property.

The change in the probability of formation of defects with increasing x-ray energy mentioned in the postulates explains the large changes in the various curves after the 300keV x-ray irradiation.

One must realize that the x-ray irradiations have not been repeated as yet, therefore these postulates may change somewhat as more data are accumulated.

Having seen that the above postulated triple defect model satisfies the experimental results, one wonders if other models will. Starting with single defects, we see that they will explain various portions of the data but none will explain it all. For example, hole traps would explain the intrinsic range of the conductivity for 150keV and 250keV x-ray irradiations but not the strong decrease in the photoconductance found after 300keV x-rays or any of the glow curves. If one replaces the hole trap with electron traps this will explain some of the glow curves but not the initial increase in the spectral response. Similar incorrect examples can be found for double defect models. A different triple defect model could have the recombination centers near the surface and the hole and electron traps in the volume; this however would explain shifts

in conductance just opposite to those we have found experimentally. Thus we conclude that our postulated model of three defects is the simplest model capable of explaining all the experimental results.

4.3 Microscopic Model

The following discussion excluded the actual surface due to lack of knowledge about it. Experiments are currently being planned to study the surface of CdS crystals in ultra-high vacuum.

No conclusive experiments have been carried out as yet to determine the nature of the defects formed by x-ray irradiation in CdS, however by assuming intrinsic defects and simply laying out all the possible combinations of Cd and S defects, i.e. vacancies, interstitials, associates, etc., possible in the CdS lattice one can select the most probable defects when geometry and electrostatics are taken into account. For purposes of simplicity only two center associates of nearest and next nearest neighbors will be considered.

Donors would act as electron traps; two different donors would be a Cd interstitial or a S vacancy. Formation of a sulfur vacancy requires the removal of a S atom; this is improbable due to the large size of the sulfur atom. Therefore it is concluded that a Cd interstitial is the most probable electron trap.

As a Cd interstitial is formed one also forms a Cd vacancy thus creating a hole trap. Near the surface it is believed possible to remove the Cd atom and S atom entirely "from the crystal" thus leaving a larger percentage of hole and electron traps than in the bulk.

One now questions the validity of assuming a range or very closely spaced band of discrete values of energy for trapping and trap emptying as in postulate c. This may be feasible when one recalls that the initial glow curves show no one trap energy predominating but more correctly a continuum of trapping levels.

Recombination centers consist of donor-acceptor associates, i.e. Cd interstitial-vacancy, S interstitial-vacancy, S-Cd interstitials, S-Cd vacancies. The probability of the latter two forming close enough together to interact is small. The probability of forming the first associate is not as small as the latter two but smaller than the second associate because of the small size of Cd, it can travel through the lattice quite easily with thermally acquired energy and away from its vacancy. The most probable recombination center is therefore the S vacancy-interstitial. Due to the large size of the sulfur atom it does not diffuse through the lattice freely and can easily be the next nearest neighbor to the vacancy.

5. ANNEALING

5.1 Experimental Results

Previous work with other CdS crystals has shown that a temperature vs. time curve as shown in Figure 4-5 will anneal some defects in CdS crystals. For reasons discussed below the flat region located at about 170°C should be lowered to about 135°C for this crystal as shown by the dotted line. To anneal the crystal it was heated to a given temperature, kept at this temperature for five minutes, and then cooled to room temperature following the solid curve in Figure 4-5

The extrinsic range of the spectral response and the glow curves return to the value they had after 250keV x-rays when annealed at 100°C maximum temperature. Further increases in the annealing temperature maximum to 150°C and 200°C produce only small increases (approximately 5%) in the glow curve conductivity, see Figures 4-6, 4-7 and 5-8. As the annealing temperature maxima are increased to 250°C, 300°C, and 330°C, a drop of approximately one-half an order of magnitude is seen in all the glow curves.

In the extrinsic range of spectral response a rise in photoconductance is seen with each rise in annealing temperature, Figure 4-9. The intrinsic range of the spectral response is seen to decrease after 200°C maximum annealing temperature. However at 250°C

maximum annealing temperature there is once more a significant increase in the intrinsic conductance. Further increases in the annealing temperature maxima to 300°C and 330°C produce decreases in the intrinsic spectral response.

5.2 Discussion of Annealing

We have seen that some of the x-ray induced defects anneal out at 100°C. Previously we assumed that these x-ray induced defects were due to sulfur vacancy-interstitial recombination centers. Since these two defects must be close together to act as a recombination center it is quite reasonable that the associate should return to a normal S atom with the addition of a little thermal energy. It was further assumed that the other defects were due to the dislocation of Cd from its normal lattice site; the probability of these vacancies and interstitials finding each other is small; therefore their effects remain.

The small initial increases in the glow curve ($Low T$) conductances may be attributable to ordering of the lattice whereby the electron scattering is reduced and mobility is increased. The later large drops in glow curve conductances might be connected to an increased number of recombination centers at first glance. However then they should also affect the spectral response; this is not the case as is seen in Figure 4-9. Therefore

one must conclude that the reduced glow curve values are due to a reduction in the electron traps in the energy range of 0.3-0.6eV in the crystal, (the energy being calculated by the equation first formulated by Randall and Wilkins;⁵ $E \sim 25kT$.)

The increase in conductance in the extrinsic range of spectral response with increasing annealing temperature can best be explained by assuming an increasing number of thermal defects in the crystal in this energy range, i.e. acceptors. The maximum number of these defects appears to have an energy at approximately $E_c - E_a = 2.0\text{eV}$. This would be sufficiently far enough into the extrinsic range so as not to influence the band gap conductivity. The decrease of the conductance in the intrinsic range of the spectral response can be attributed to the thermal defect centers which increased the conductance in the extrinsic range. In the intrinsic range the thermal activators which previously acted as hole traps are now acting as recombination centers, since the quasi-Fermi level for holes has been lowered near the surface by increasing the concentration of holes in the valance band.

It is known that oxygen acts as an acceptor in CdS and in a region with a high concentration of holes, the surface being illuminated with the light of wavelength shorter than the band energy, it is possible that these acceptors act as recombination centers also.⁶

Thus if the oxygen were thermally desorbed from the surface, we would observe an increase in surface photoconductivity due to less oxygen activated recombination center. Therefore, it is postulated that the increase in the intrinsic photoconductivity is due to oxygen desorption occurring approximately 250°C maximum annealing temperature, since the crystal has never been raised to this temperature before.

Further increases in the annealing temperature maximum to 300°C and 330°C produce decreases in the intrinsic spectral response which can again be attributed to the shift in the quasi-fermi level by which an increased number of activators and hole traps become recombination centers.

6. Photochemical Effects

After heat treatment at 300°C and annealing, photochemical reactions have been found to be greatly enhanced. Further discussion does not seem appropriate at this time.

7. 300 KV Irradiation at -185°C

The spectral response curves at the beginning of this program showed some structuring in the extrinsic range and what appeared to be a well pronounced peak between 640 and 660mμ.

The spectral response and glow curves for the 300keV x-ray irradiation at -185°C are given in Figures 4-10 and 4-11. The irradiation duplicated previous ones with the exception that the crystal was held at liquid nitrogen temperature from the beginning until the glow curves were taken immediately following this.

7.1 Experimental Results

1. A general increase in conductance in the glow curves which is especially pronounced in the region from 170°K to 260°K was observed.

2) The spectral response curve showed greater conductance in the extrinsic range and at the peak (498 - 500 m μ at -185°C).

3) No change in the intrinsic portion of the spectral response curve.

7.2 Phenomenological Explanation.

It is proposed that similar to the irradiations at room temperature, there is an increase in the number of electron traps. This is inferred by the increase in conductance in the glow curves. The increase is especially pronounced in the region between 0.4 and 0.56 eV from the conduction band.

The increase in conductance in the extrinsic region is attributed to an increase in the number of hole traps.

It is suspected that the recombination center produced in the bulk of the material at room temperature are not found at liquid nitrogen temperature. However some recombination centers are produced near the surface.

Therefore, basically the same phenomenological model is used here as was used for irradiation at room temperature.

7.3 Microscopic Model

The additional information gained from this experiment concerned the recombination centers. If we choose the $S_O S_{\square}$ associate as the most probable radiation produced recombination center at room temperature, then sufficient energy is ~~not~~ available to produce this de-

fect at -185°C . This is reasonable since less thermal energy is available from the lattice and we are working very near the threshold energy for removing an atom from a lattice site. Recombination center production in the near surface region may be more energetically favorable because expansion of the lattice in the direction normal to the surface to accomodate sulfur interstitials requires less energy than expansion in the bulk of the material.

7.3 Annealing

The crystal remained at room temperature and in darkness for six days and then a spectral response curve and glow curves were taken as shown in Figures 4-10 and 4-11. The glow curves approached their pre-irradiation values. The conductance in the extrinsic region of the spectral response curve has decreased while the intrinsic region has increased.

The electron and hole traps are assumed to have already begun to anneal out at 25°C . The annealing out of recombination centers near the surface would account for the rise in the intrinsic region. The higher value of conductance in this region could be the result of ionized gases at the surface which were not present before irradiation.

Figures 4-12 and 4-13 show the changes in spectral response and glow curves for various annealing temperatures. Annealing at 100°C , 150°C and 200°C produced a parallel shift to higher photoconductance.

in the spectral response curves and what appears to be a parallel shift of the glow curves toward higher conductance plus an increase in the glow peak occurring at $\sim 150^{\circ}\text{K}$. The largest change occurred after annealing at 150°C .

The changes are thought to be attributable to the thermal dissociation of an associate which is acting as a recombination center. The rise of the glow peak at $\sim 150^{\circ}\text{K}$ may be due to one of the by-products of this dissociation.

After the 200°C annealing, the previously mentioned measurement to determine if photochemical reactions were present was made and upon re-running the 200°C spectral response curve after illuminating the crystal at room temperature, the photoconductance was found to have been decreased by approximately one order of magnitude. Subsequent annealing at 200°C shifted the spectral response curve to higher conductance, however complete annealing of the photochemically produced defects was not accomplished.

Annealing at 250°C and 300°C produced only small changes in the respective curves.

8. Present work

At the present time measurements are being made in regard to a 300keV x-ray irradiation at room temperature. Subsequent to this, x-ray irradiation at :

liquid nitrogen temperature will be repeated. It is hoped that these data will produce not only information regarding reproducibility, but new information regarding radiation defects as well since we are now in a position to aim for certain changes in defect structure which were indicated at our first occupational investigations.

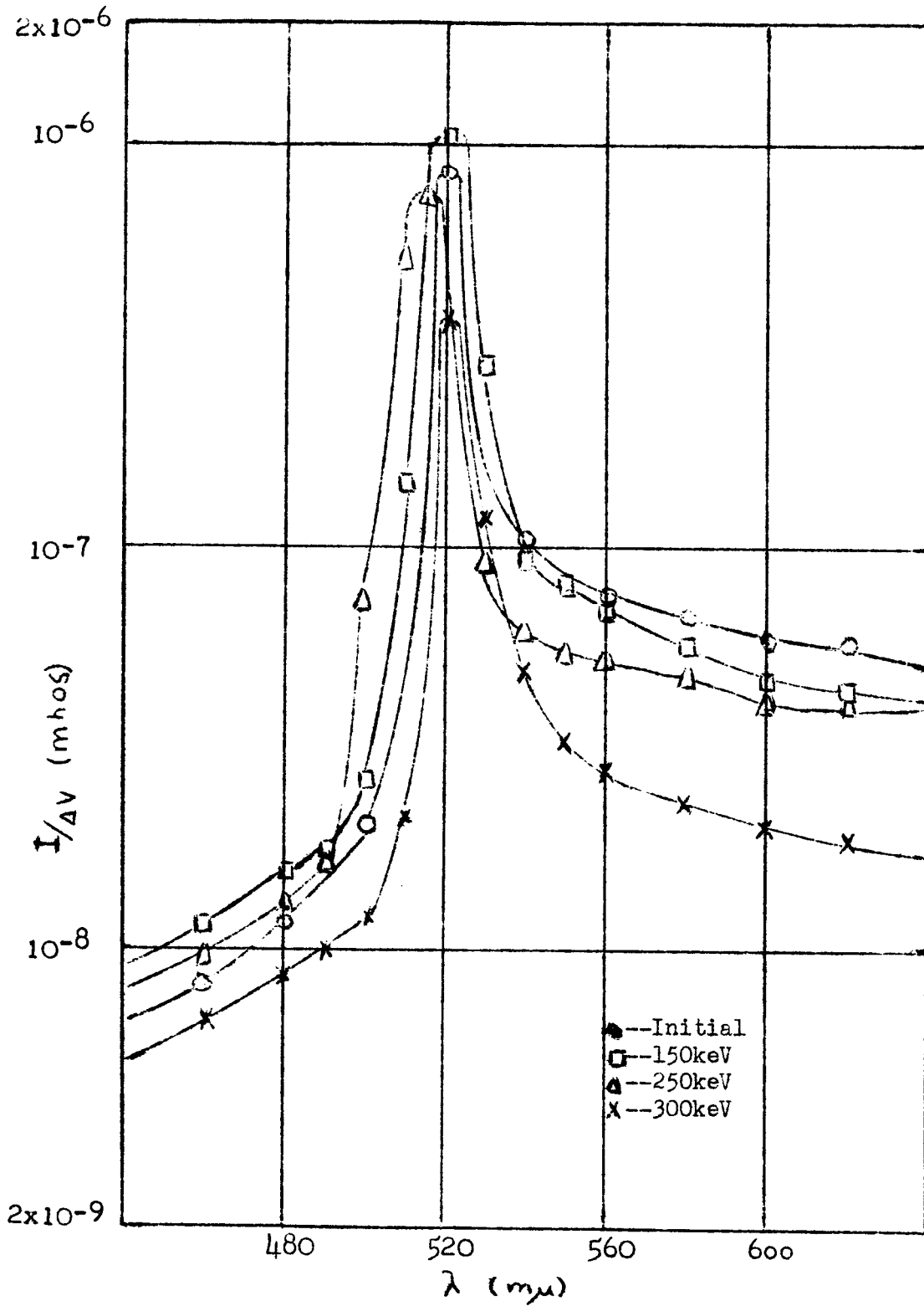


Figure 4-1. Spectral Response, before and after x-rays at room temperature.

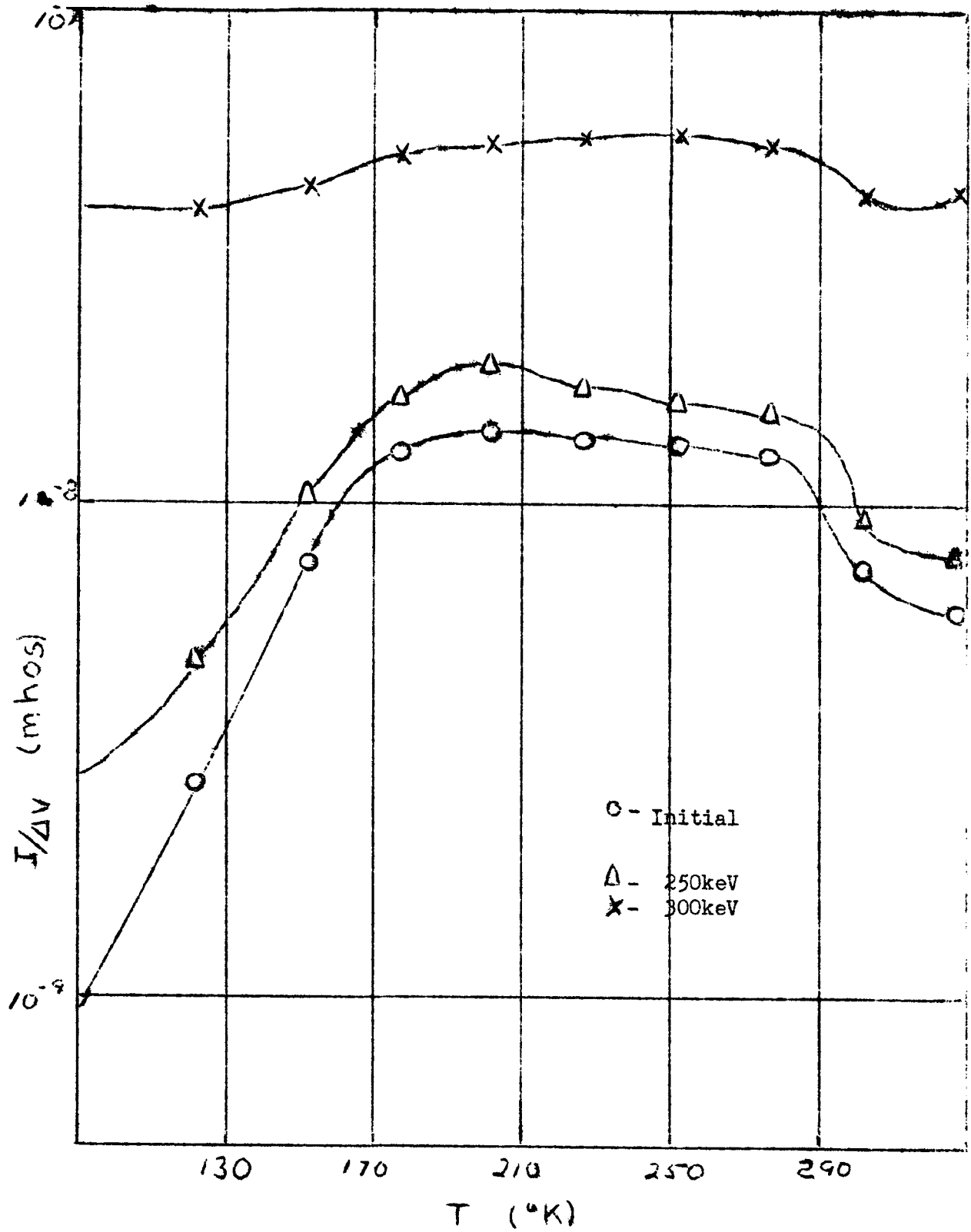


Figure 4-1. Glow Curves 510mμ illumination at liquid N₂ temperature: before and after x-rays.

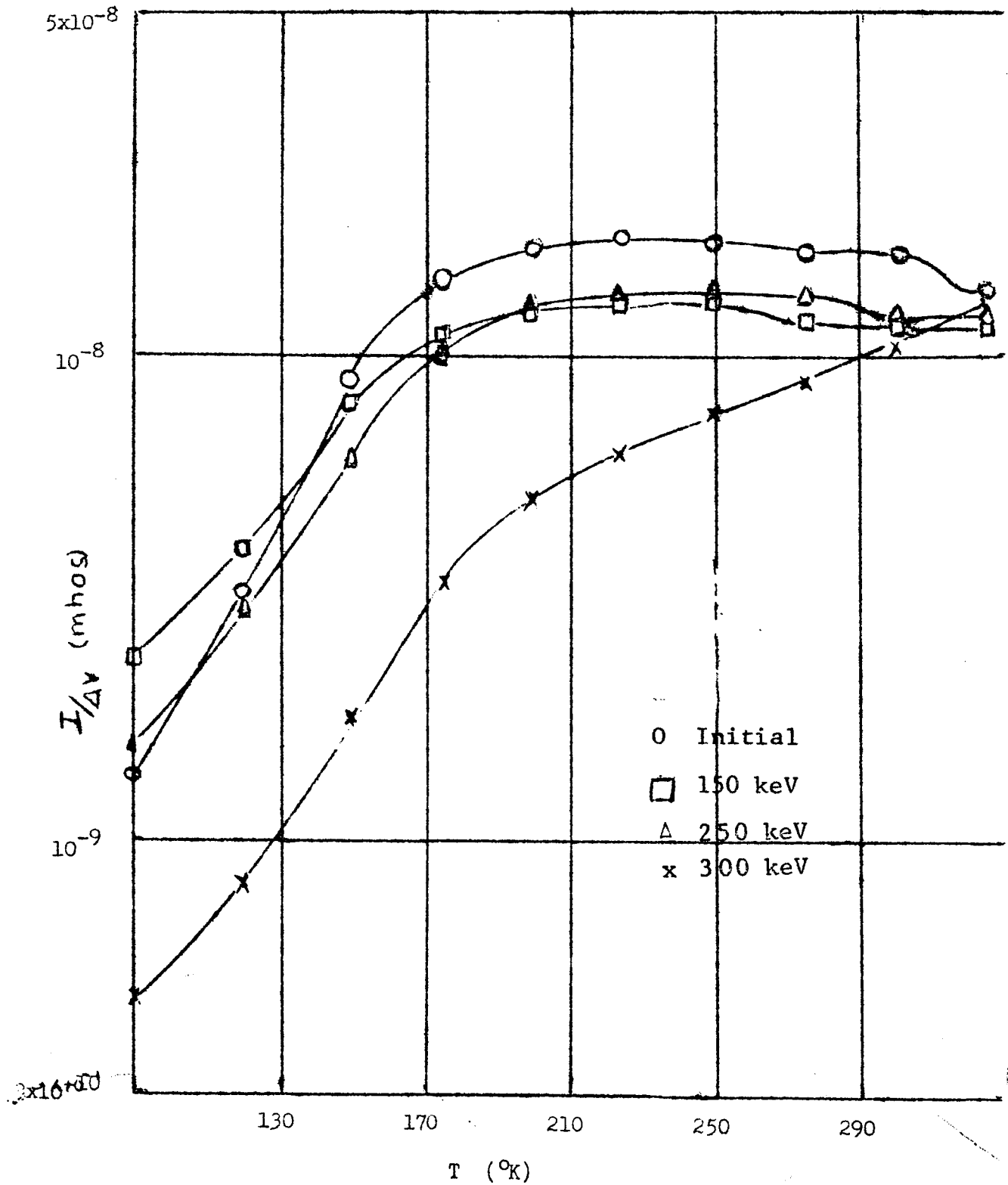


Figure 4-3 Glow Curves 650mp illumination at room temperature before and after x-rays.

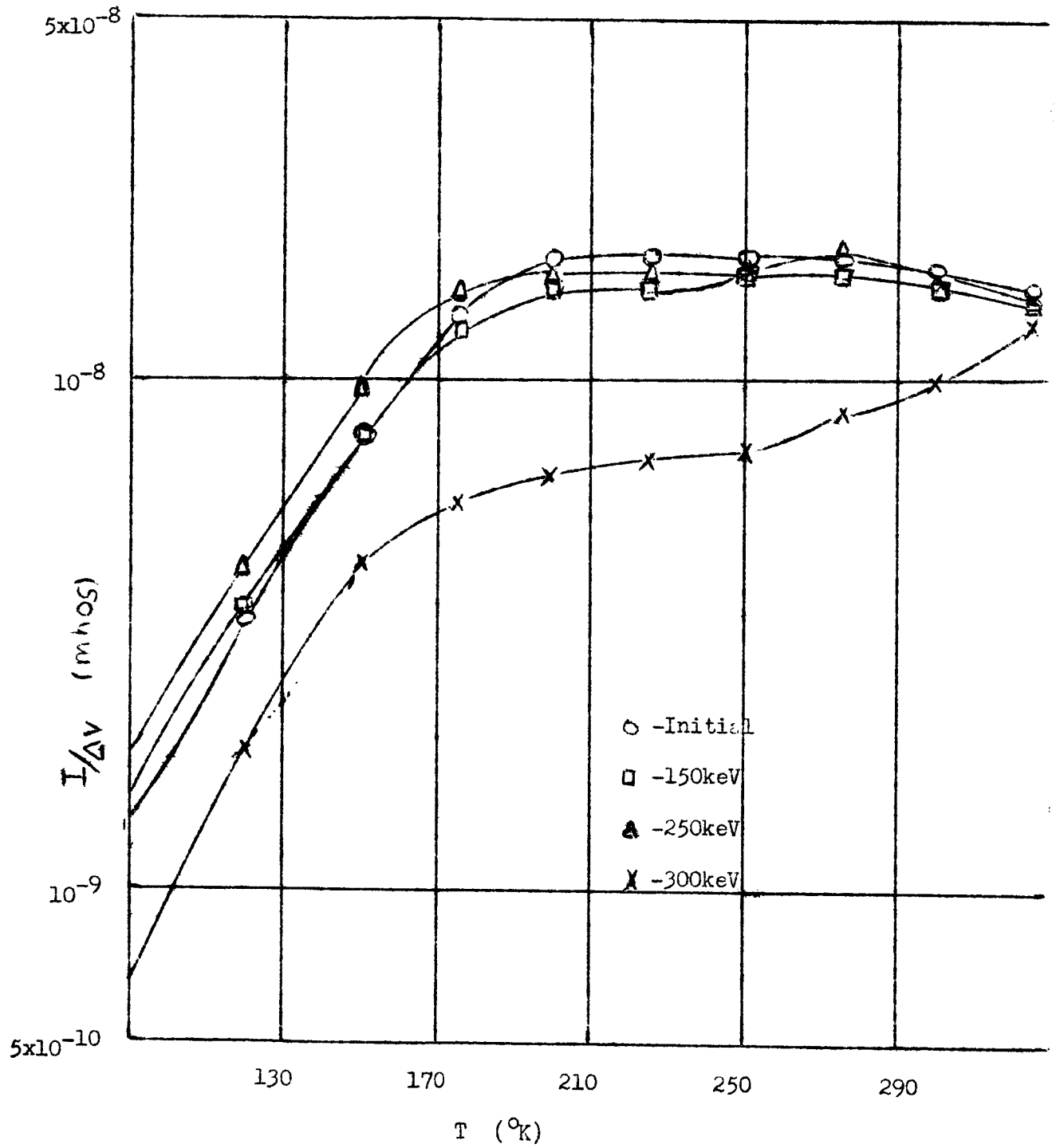
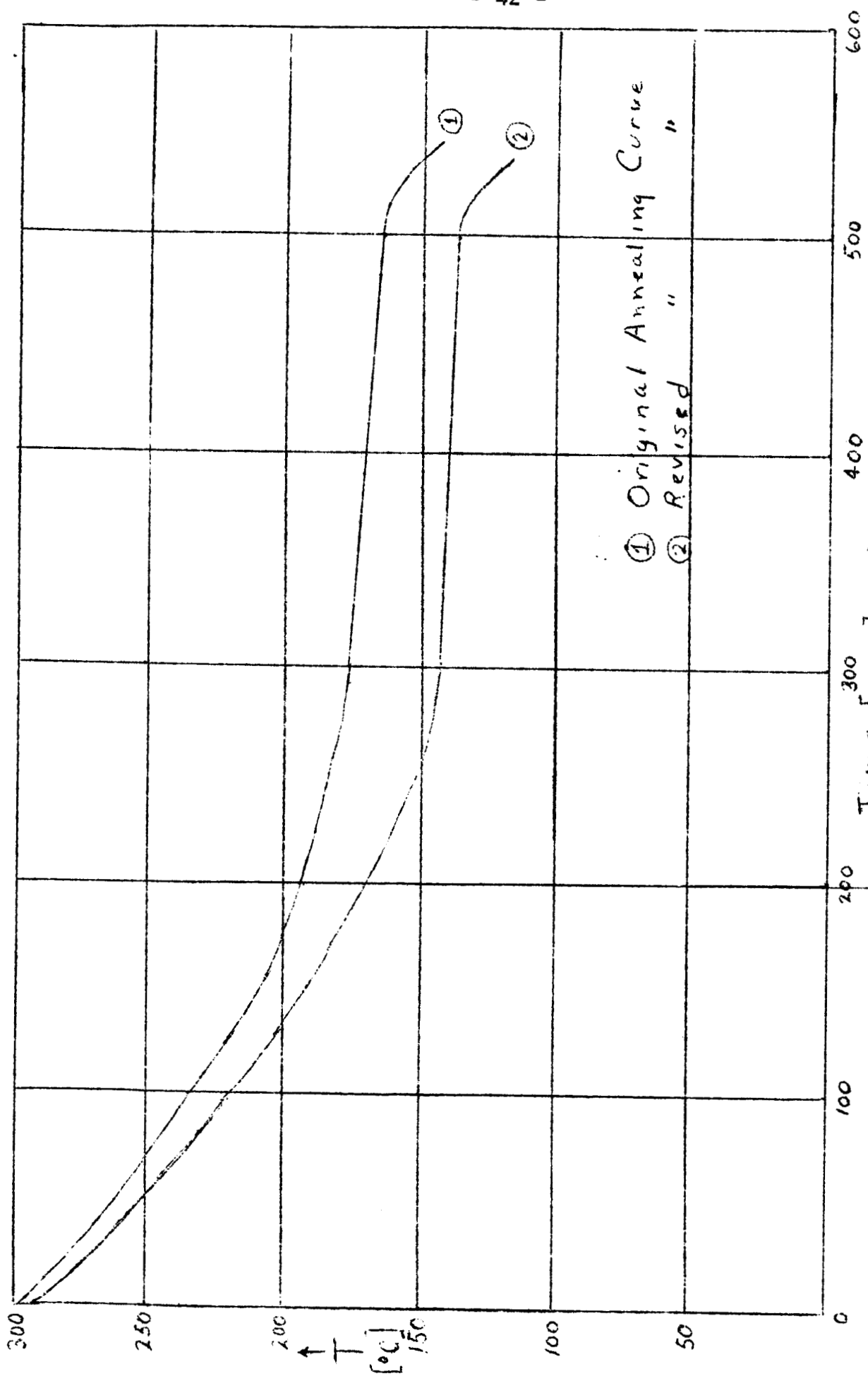


Figure 4-4 Glow Curves 650mu illumination at liquid N₂ temperature before and after x-rays.



① Original Annealing Curve
② Revised "

Time [min] →

Figure 4-5.
Annealing Curves

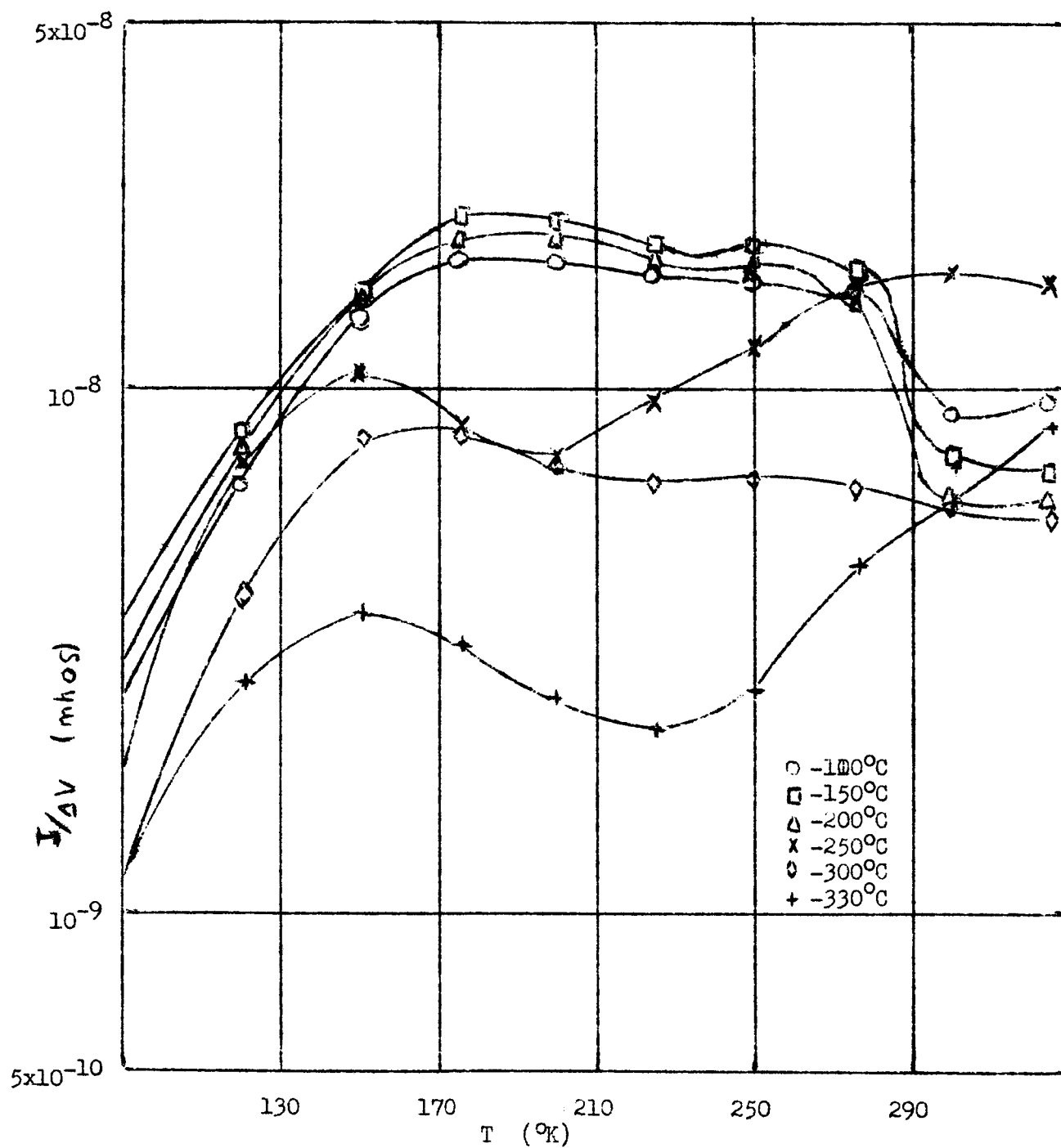


Figure 4-3. Glow Curves 510m μ at liquid N₂ temperature after annealing.

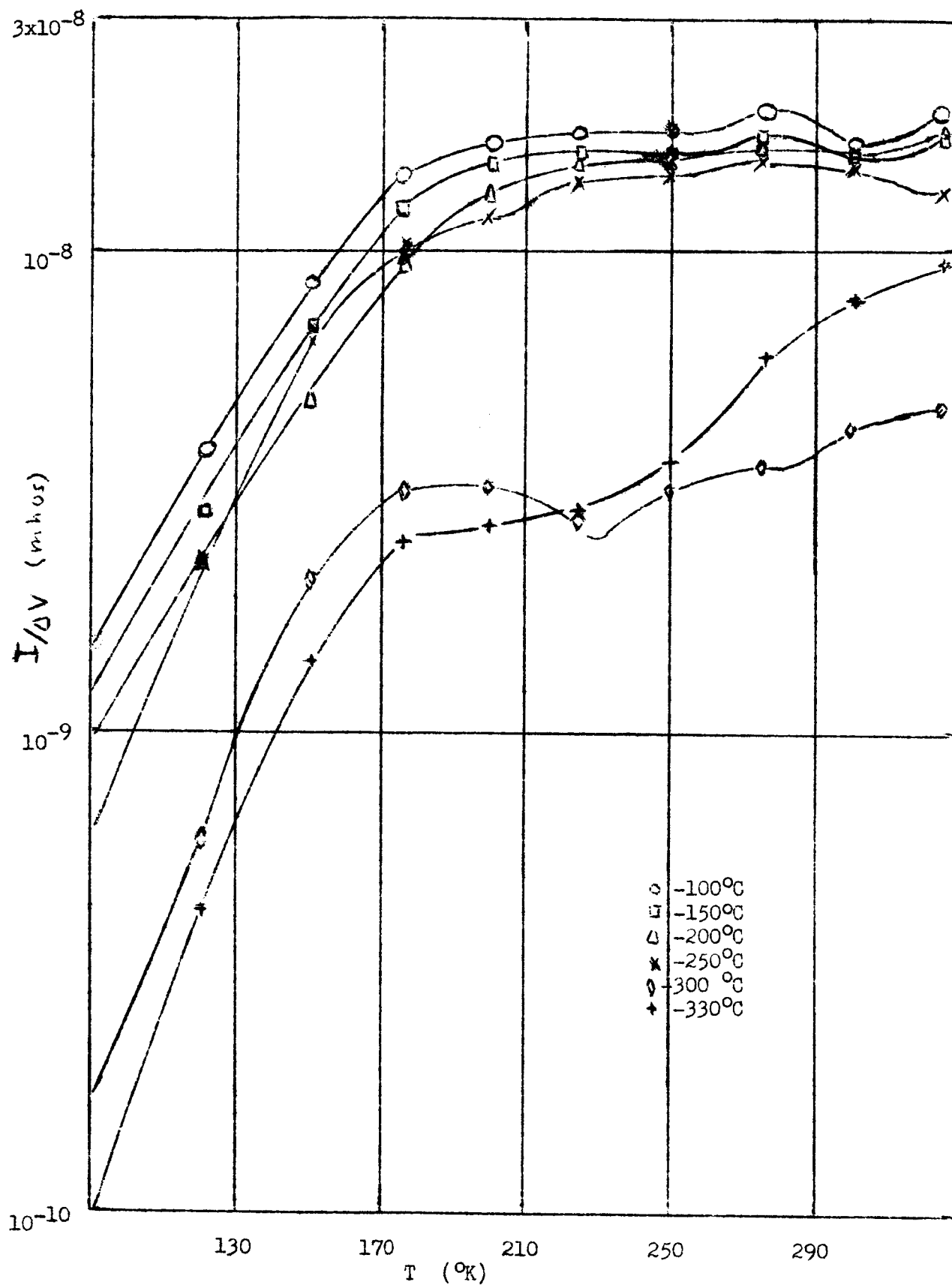


Figure 4-7. Glow Curves 650mμ illumination at room temperature after annealing.

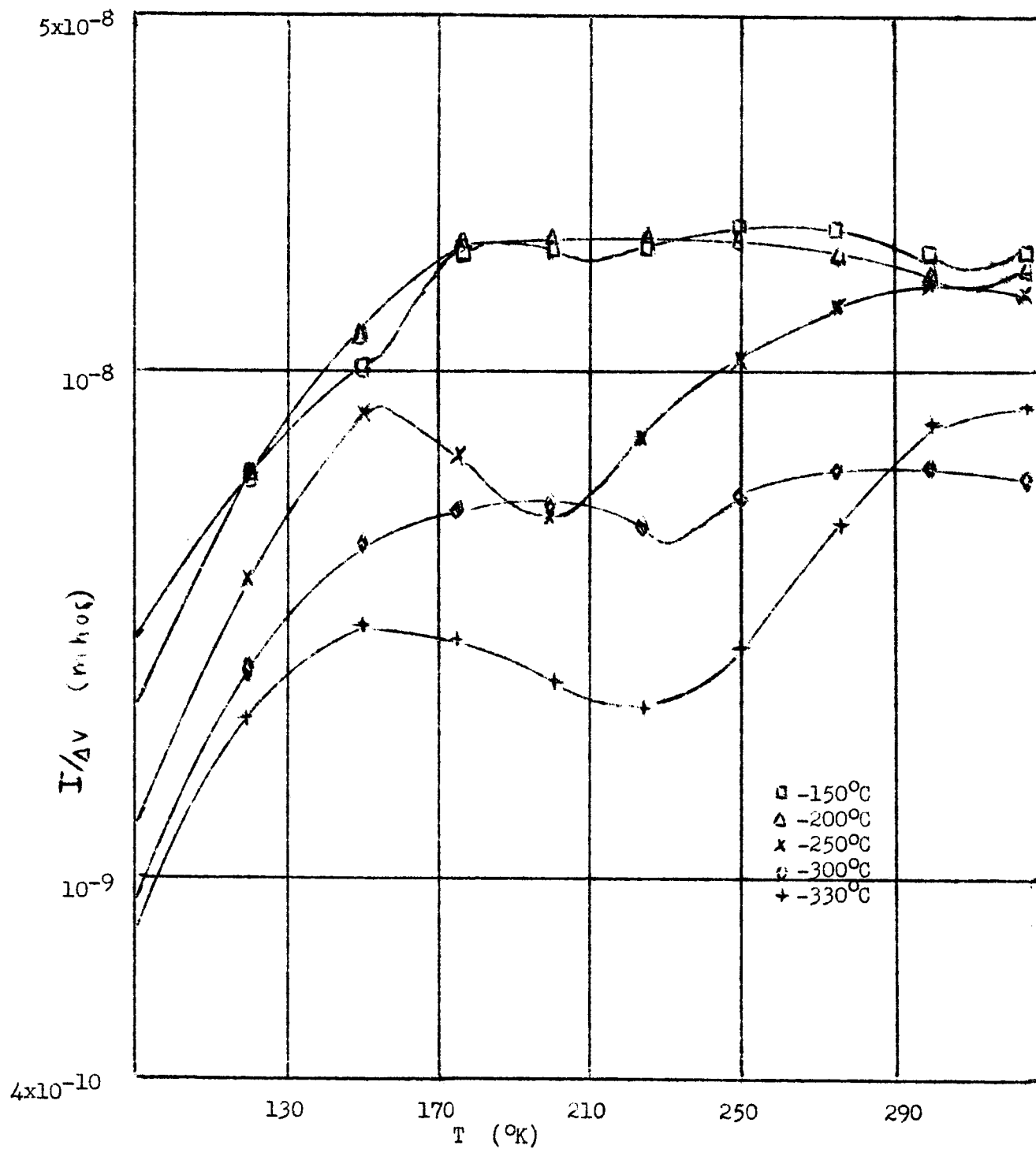


Figure 4-8 Glow Curves 650mμ illumination at liquid N₂ temperature after annealing.

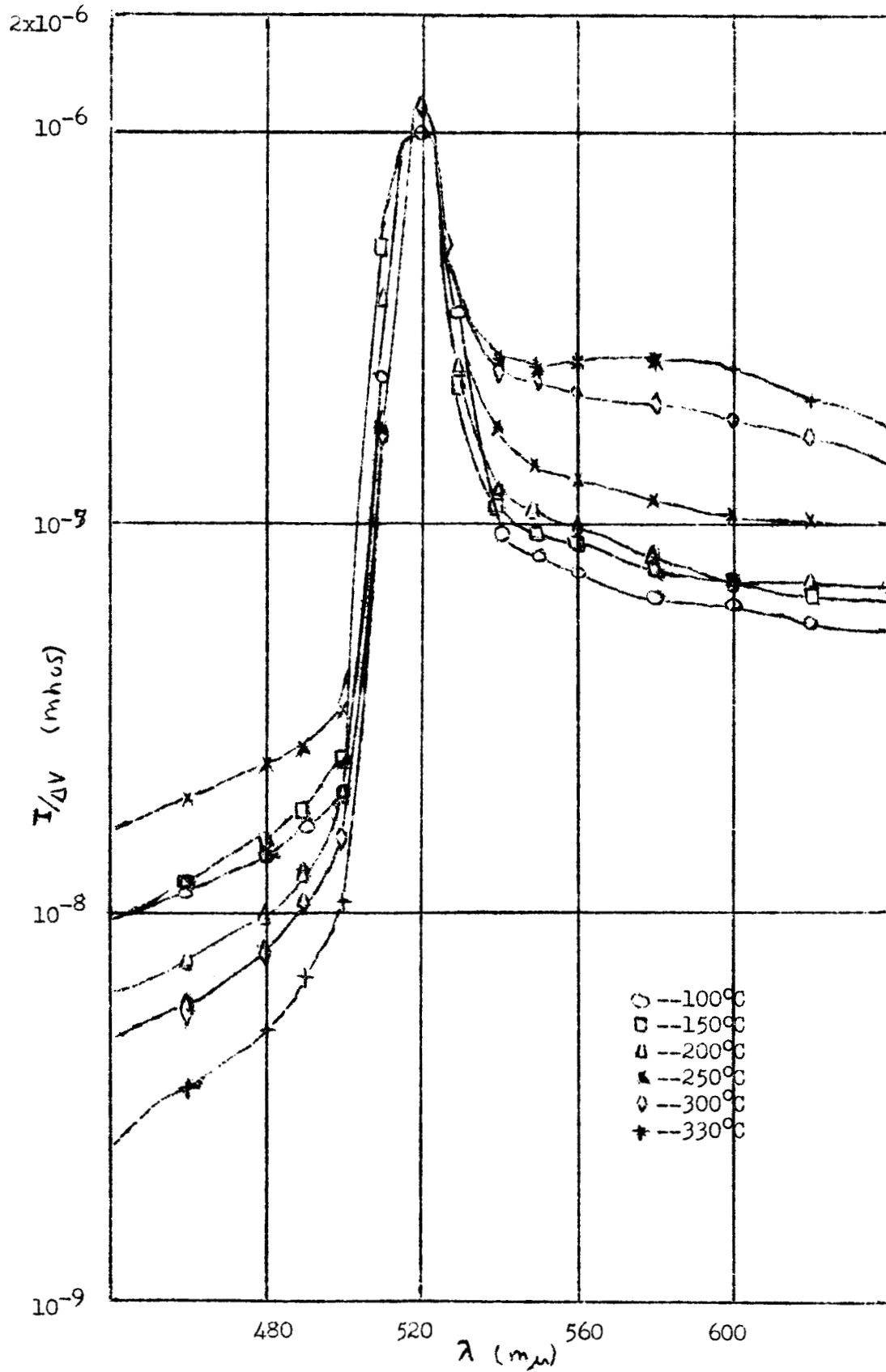


Figure 4-9 Spectral response after annealing.

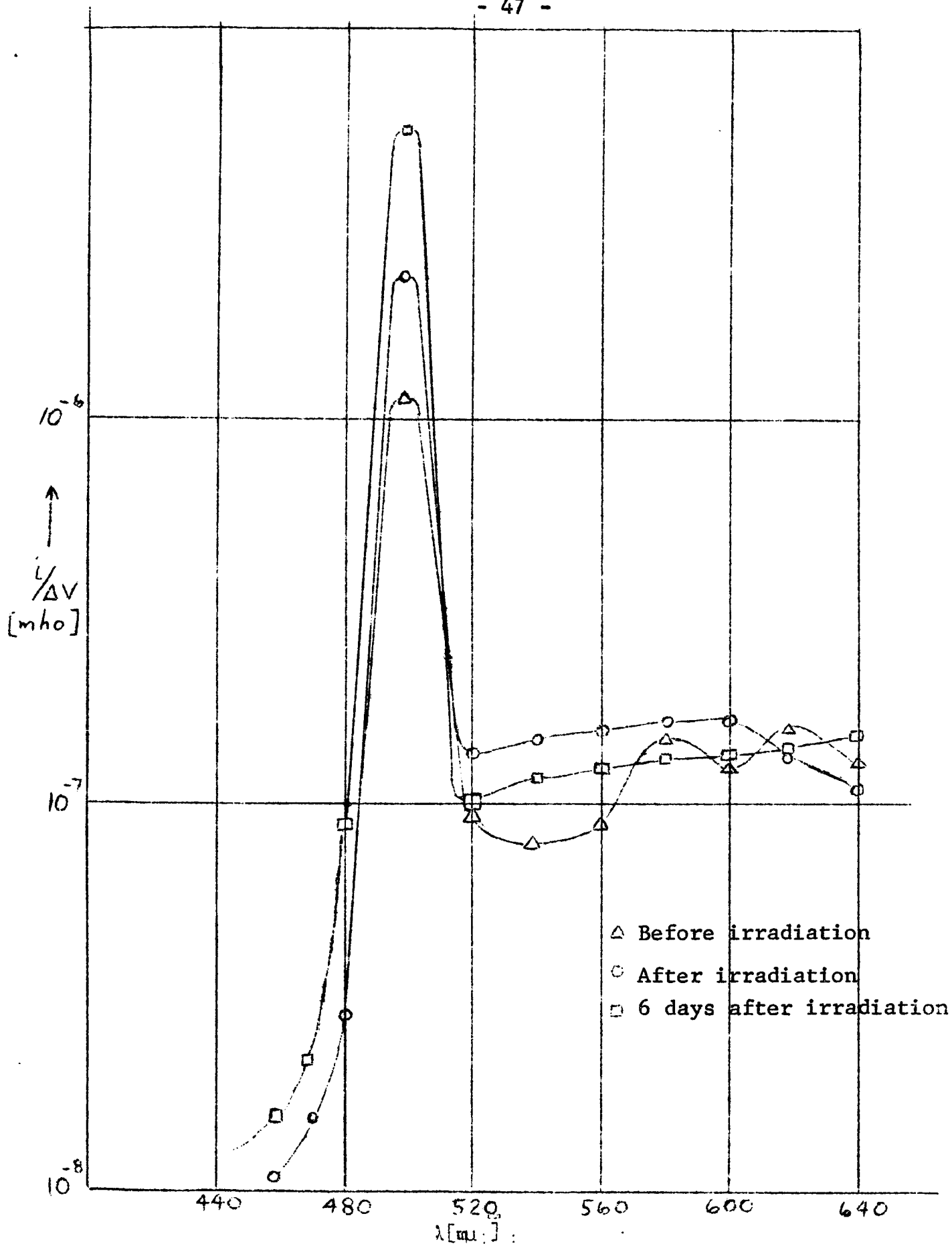


Figure 4-10 Spectral Response Curve

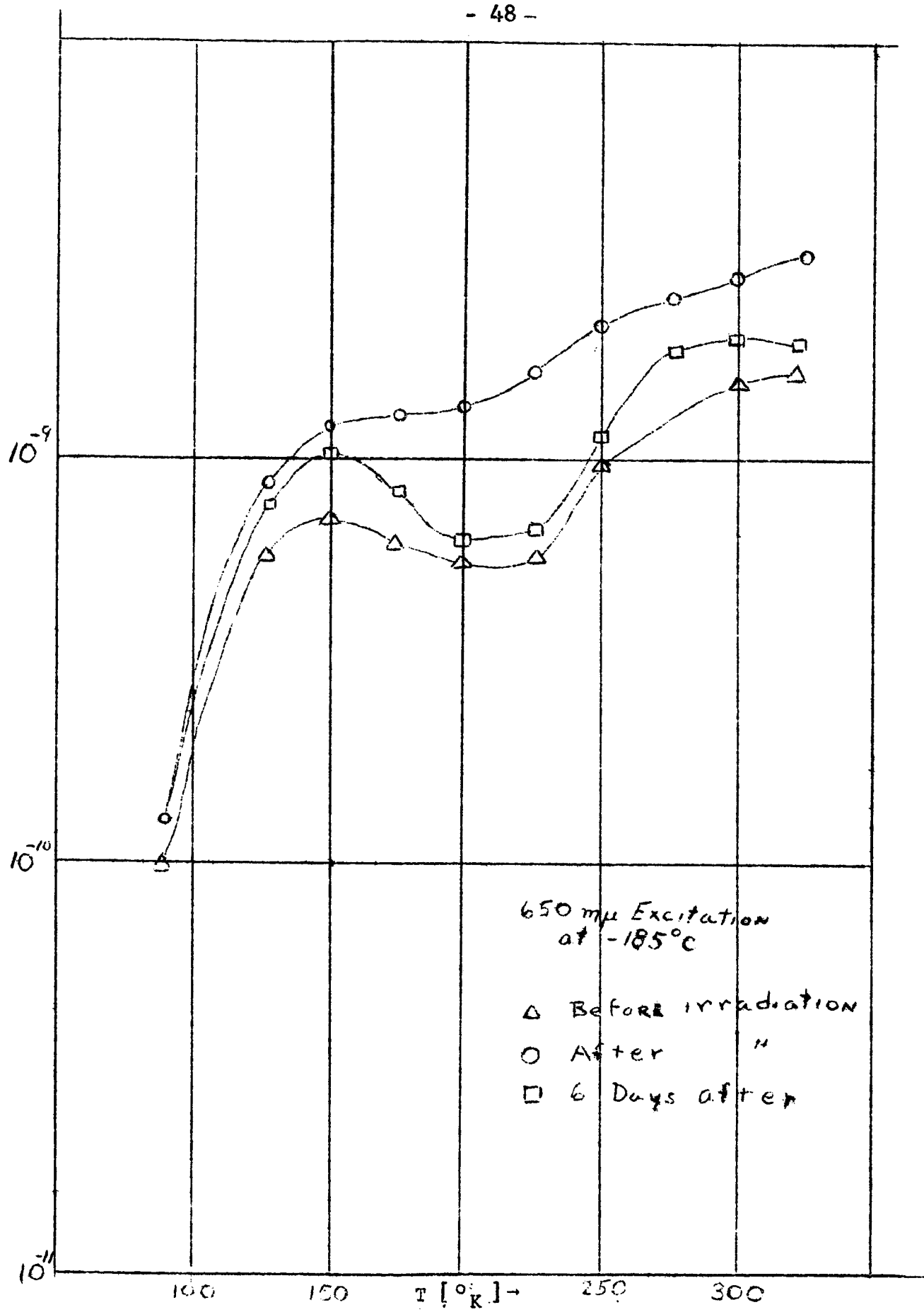


Figure 4-11-1-Glow Curves

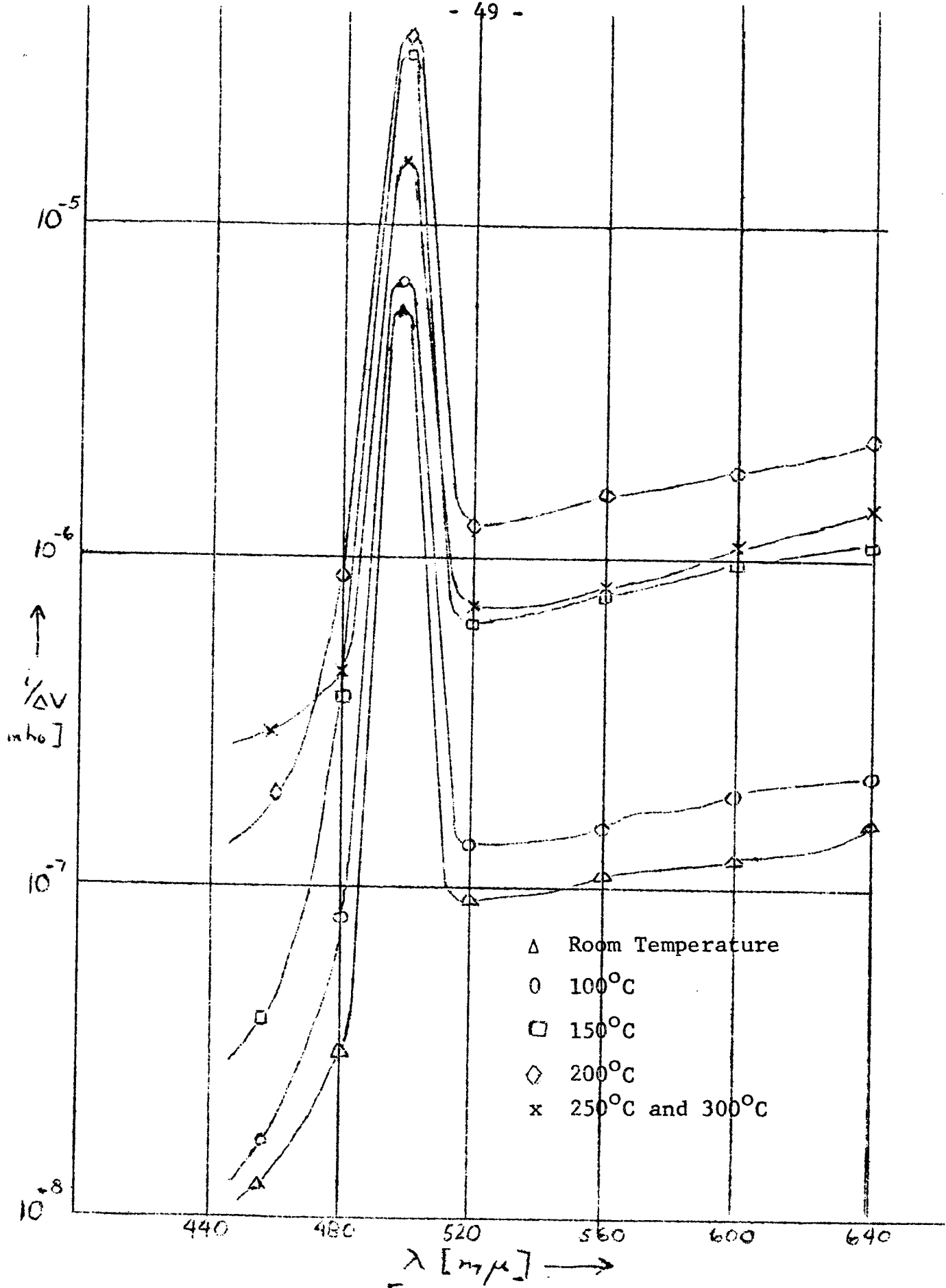


Figure 4-11
Spectral Response Curve For Annealing

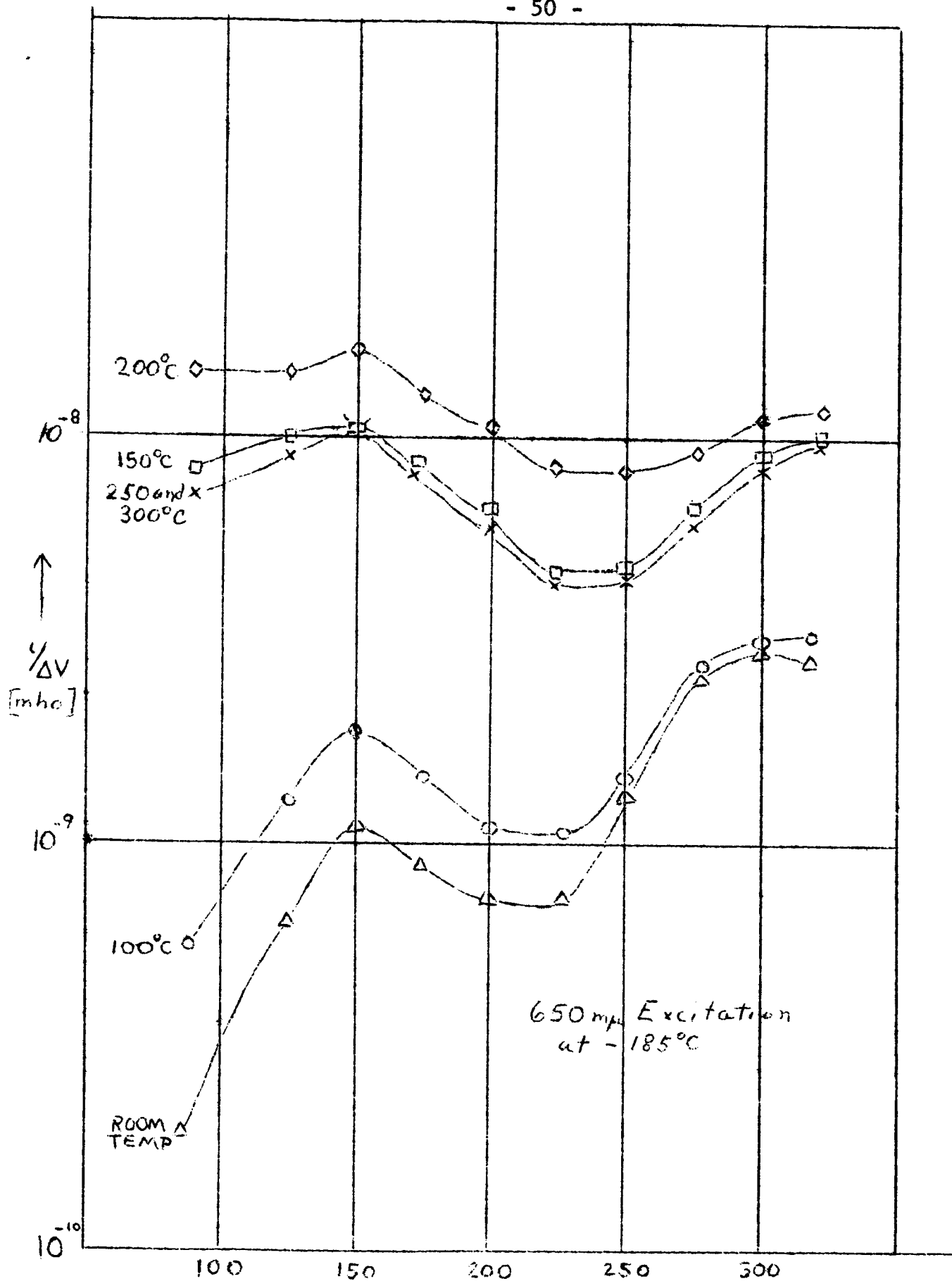


Figure 4-13
Glow Curves

Ad:5

EFFECTS OF SULFUR HEAT TREATMENTS ON
THE DARK CONDUCTIVITY OF CdS SINGLE CRYSTALS

The effect of sulfur vapor on the dark conductivity of CdS has been studied in the temperature range of 300° - 750°C for six CdS platelets. In general, the dark conductivity has been found to decrease with increasing sulfur vapor pressure. The stationary dark current as a function of sulfur vapor pressure can be represented by:

$$i_{\text{stat}} \sim P_s^{-1/m} \text{ where } m = 2 \times \begin{array}{l} \text{the average "size"} \\ \text{of the sulfur molecules} \end{array}$$

The crystals had two large gold and chromium, or gold electrodes evaporated on one surface separated by a distance of 1.5 - 2 mm. Two crystals were mounted on a quartz crystal holder with Pt-Rh wire serving as pressure contact. The crystals were located in one chamber of a quartz vessel which consisted of two chambers 30mm x 120mm long, joined by a quartz capillary tube 120mm long. Contact wires and thermocouple wires passed out of the tube through smaller quartz pipes and were sealed with sealing wax. Spectroscopically pure sulfur was placed in the other chamber. An exhaust tube connected the sulfur chamber to a vacuum system. After melting and outgassing the sulfur for three hours at a temperature of 150°C under vacuum, the exhaust tube was sealed at a pressure of 10^{-4} Torr. The vessel was then placed in a double oven where the temperatures of the crystal and the sulfur could be regulated independently. The partial pressure of the sulfur was

calculated from the temperature of the sulfur. The temperature in the crystal chamber was always higher than in the sulfur chamber.

Results obtained from the first two crystal sets indicated that some of the technique described above was not completely satisfactory. While the use of a gold-chromium contact as opposed to a pure gold contact improved the rigidity of the contact, any chromium exposed to the sulfur atmospheres would react chemically with the sulfur, which is very corrosive to all non-noble metals. The first two contacts disappeared after sulfur heat treatments at 550°C. The second set of contacts were badly discolored. Also, because of the manner in which the wires were led out of the vessel, small leaks in the wax seals became very troublesome, especially since a typical program of measurements requires a two month period.

These difficulties led to the development of a different method of contacting the crystals using pure gold which has been reliable to temperatures up to 750°C and a method for continuous pumping under heat treatments. Evaporated gold contacts are used as described. A spherical drop of gold is fused onto the end of the Pt-Rh pressure contact to minimize the danger of scratching. A piece of leaf gold is placed between the pressure contact and the evaporated electrode to insure that there is no scratching. A new containing vessel has been constructed which can be pumped continuously while measurements are being made. The exhaust tube is connected to an oil diffusion pump through a cold trap. The crystals are heated to a temperature of 400°C to

outgas the crystal portion of the tube. Then the sulfur is heated to a temperature of 160°C . At this temperature the sulfur begins to diffuse into the exhaust tube. By cooling the exhaust tube the sulfur condenses and forms a plug which prevents the sulfur from contaminating the rest of the system; small leaks in this plug allow further pumping action.

Results

Using the new system the dark conductivity has been measured as a function of sulfur vapor pressure and the temperature dependance of the dark conductivity has been studied after sulfur heat treatments of approximately one hour at different temperatures and sulfur pressures. Figures 5-1 and 5-2 indicate some of the preliminary results obtained for one of the crystals. Additional measurements are required before a discussion of possible conduction mechanism can be undertaken.

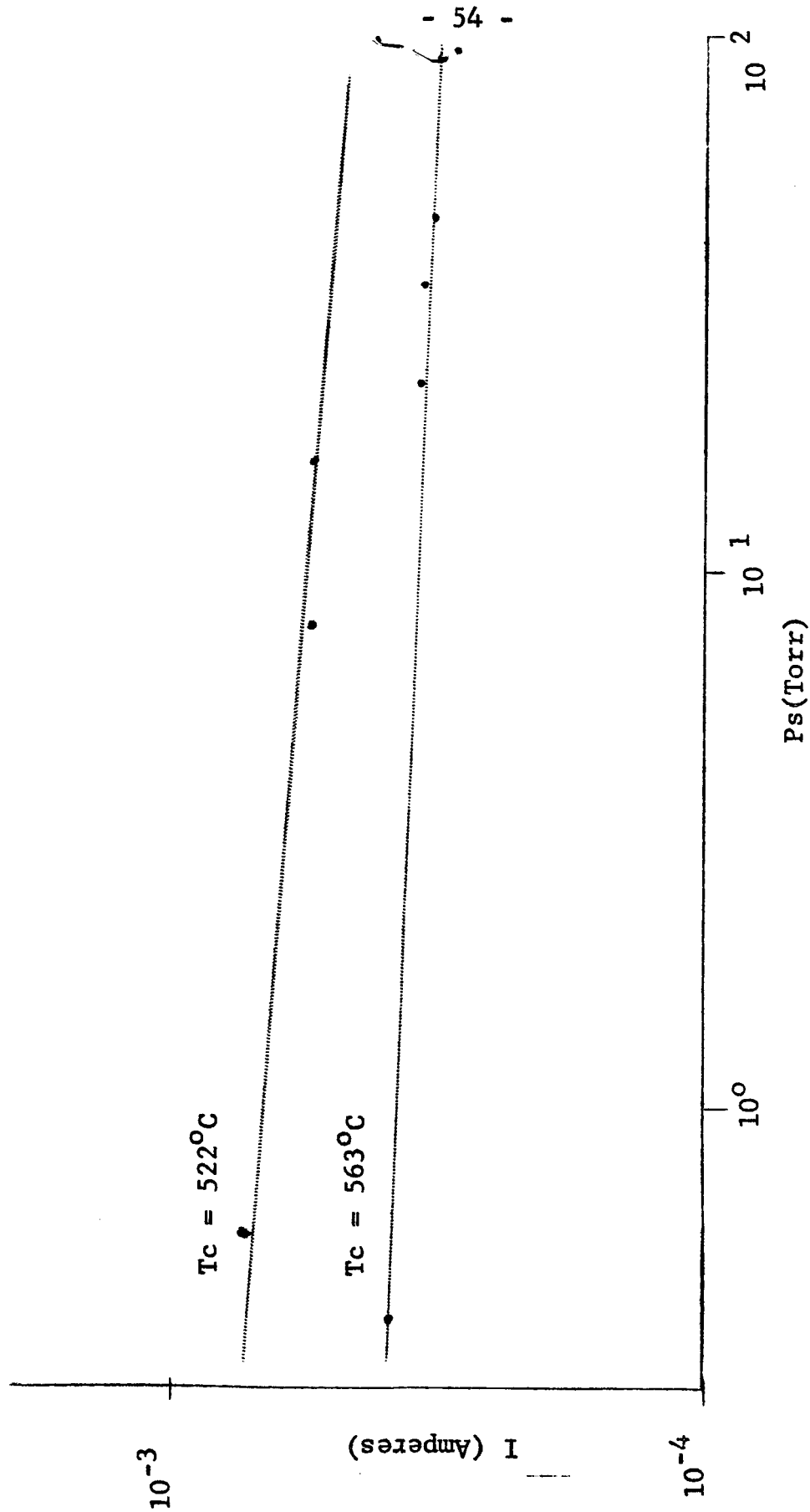


Figure 5-1: Stationary dark current as a function of sulfur vapor pressure at crystal temperature of 522°C and 563°C.

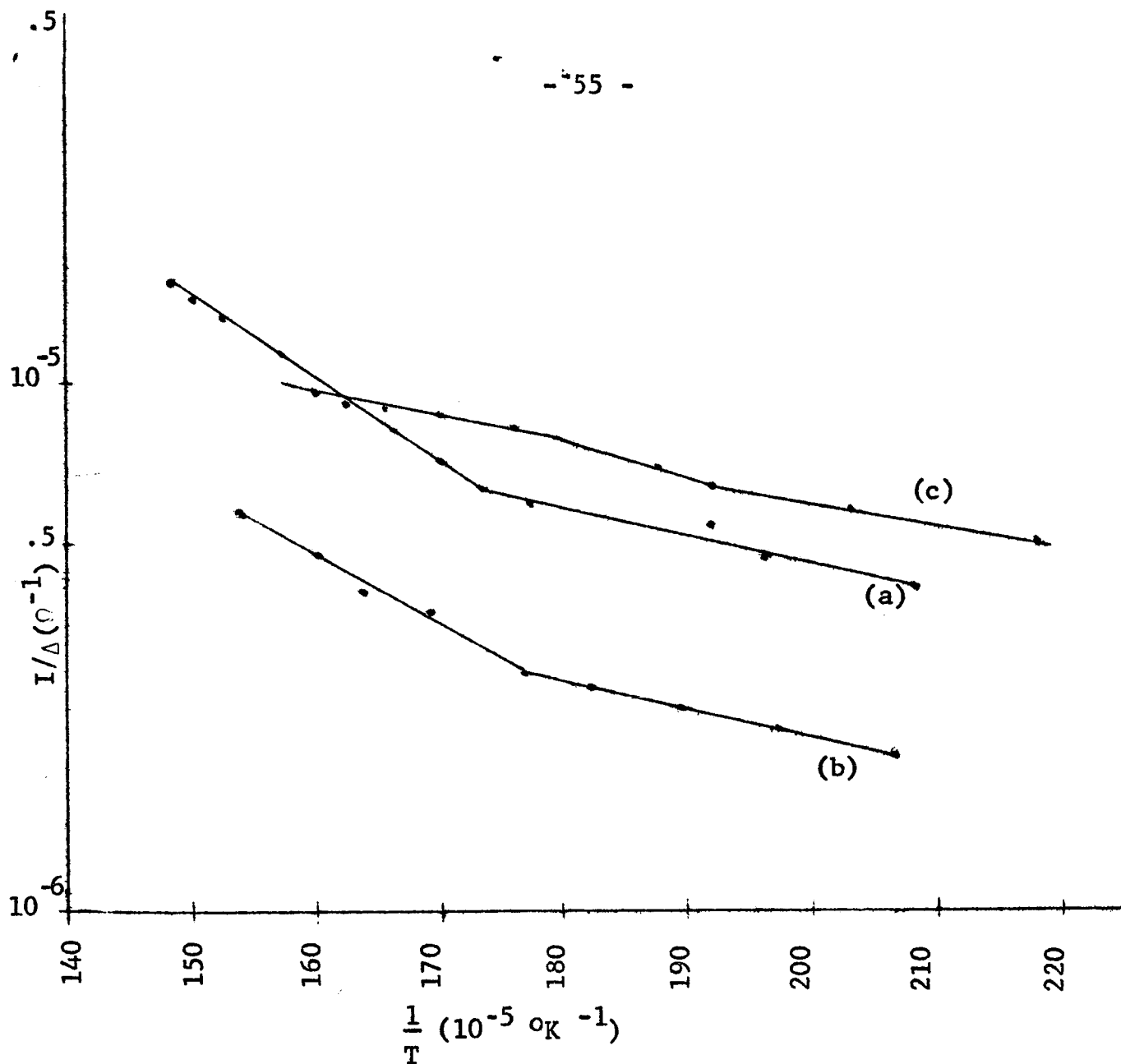


Figure 3-2: Temperature dependence of the conductance of sulfur treated CdS after heat treatments (heating rate 0.07°/sec.)

Curve	Temperature of heat treatment	Time of heat treatment	Sulfur pressure
a	400°C	15 min.	0.4 Torr
b	522°C	1 hr.	48 Torr
c	563°C	1 hr.	50 Torr